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The Analysis of QA/QC Results for AEC E128.0 Analytical Method for Adsorbable Organic Halide (A0X)

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THE ANALYSIS OF QA/QC RESULTS FOR AEC E128.0 ANALYTICAL METHOD FOR ADSORBABLE ORGANIC HALIDE (AOX)

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ABSTRACT

The quality assurance quality control (QA/QC) program for AEC Method E128.0 for adsorbable organic halide (AOX) in bleached kraft mill effluents (BKME) is discussed and evaluated in this report. Potential causes of error and the good laboratory practices (GLP) used to avoid them are outlined and discussed. Quality control test data gathered over a fourteen month period are evaluated. The method blank and daily calibration factor were found to have very little effect on method performance but the within day variance of these test results related directly to method performance. Data from duplicate analysis were analyzed and the method detection limit (MDL) of the analysis was found to be approximately 0.005 mg/L AOX as chloride. The estimated standard deviation of BKME diluted 100 times was 0.23 mg/L AOX as chloride. This method was found to be appropriate for both BKME and river waters receiving BKME. Analysis of 2-chlorobenzoic acid spikes revealed that the method efficiently recovered this compound from the matrices encountered.

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The Analysis of QA/QC Results for AEC E128.0 Analytical Method for Adsorbable Organic Halide (AOX)

C. Ian Johnson[a], Tonya Lam[a], and John Kirtz[b]

Introduction

Release of organic halide containing compounds to the environment has become a concern during the last two decades. These include both compounds used, or previously used, industrially such as polychlorinated biphenyls and pentachlorophenol, and compounds formed as byproducts in industrial processes involving the use of elemental chlorine. A large source of these latter compounds is the chlorine bleaching of kraft pulp.

There are numerous methods to determine the concentrations of organic halides in industrial effluents and the environmental samples but none is universally applicable. These methods include: Total Organic Halide (TOX)[1] for the determination of the dissolved organic halide adsorbed on activated charcoal under specific conditions; Total Organic Chloride (TOCl)[2] for the determination of organic chloride absorbed by the polyamide resins XAD-2 or XAD-4; and Adsorbable Organic Halide (AOX)[3] for the determination of total organic halide in an aqueous sample associated with the suspended solids and organic halide in solution and adsorbable on activated charcoal. This last method is applicable to pulp and paper mill effluents and internal process filtrates.

This report presents and discusses the method validation data and quality control data for the Alberta Environmental Centre method E128.0 for the determination of AOX (Appendix 4). This method was designed specifically for biologically treated bleached kraft pulp mill effluents but it has also been used to generate high quality results in the analysis of receiving waters of these effluents.[4,5]

[a] Research and Methods Development Branch, Alberta Environmental Centre.

[b] Biometrics Section, Alberta Environmental Centre.

AOX, like other organic halide methods, is a sum parameter method. It does not measure the concentration of specific compound or type of compound, but measures the concentration of all organically bonded halide. The nature of the chlorinated compounds contributing to the AOX varies considerably as follows: molecular size; toxicity; bioconcentration and bioaccumulation factors; and chemical stability and persistence in the environment. Great caution must be used when drawing conclusions or making decisions based solely on AOX data. It is best to use AOX as a "surrogate parameter", which indicates the presence of chlorinated compounds. If AOX is present in a sample, further analysis, using methods appropriate for the compounds of interest, should be undertaken. It must be noted, however, that it is entirely inappropriate to use AOX as a screening or surrogate analysis for polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) present in very low concentrations. AOX analysis is simply not sensitive enough.

General Method Description

Presented here is a general description of the method. Appended to this report is the AEC Analytical Method E128.0 for AOX. This method can be separated into three distinct operations shown in Figure 1; the adsorption on granular activated carbon (GAC); the isolation of the GAC and suspended solids by filtration; and the determination of the chloride by oxidative pyrolysis/micro-coulometric titration.

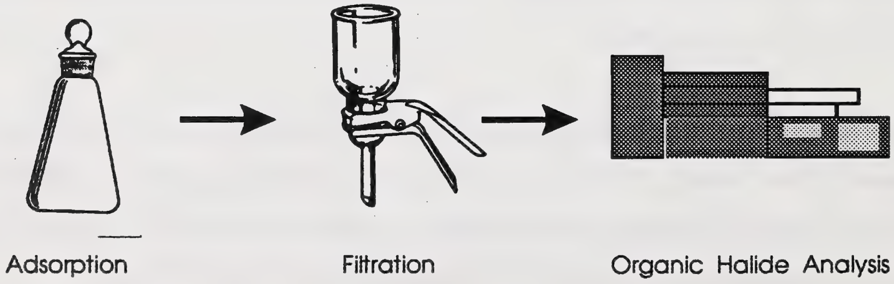

Figure 1 AOX Analysis Operations.

In the first operation, the adsorption onto GAC, sample are diluted with acidified (HNO_3) aqueous sodium nitrate and shaken with GAC in a sealed conical flask. The organic compounds present, including the organic compounds containing halogens, are adsorbed on the GAC. An aqueous sodium nitrate is used to prevent the adsorption of inorganic chloride ions as nitrate ions displace any chloride ions adsorbed to the GAC.

The GAC and suspended solids are collected in the filtration operation. Following the adsorption operation, samples are filtered through a polycarbonate membrane filter (0.4 µm pore size) and rinsed thoroughly with a nitrate solution to displace any remaining bound inorganic chloride. The filter membrane and all the collected material are set aside for organic halide analysis.

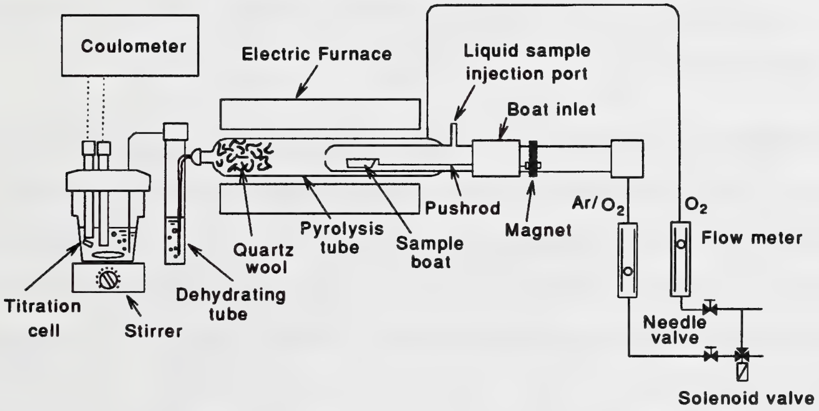

Figure 2 Mitsubishi TOX-10 Analyzer used for AOX analysis.

The organic halide analysis involves the conversion of organic halide to hydrogen halide by oxidative pyrolysis followed by the determination of the halide by microcoulometric titration. The instrument used for this operation is shown in Figure 2. The filter membrane and collected material are pyrolyzed under an oxygen atmosphere at 950°C converting the organic halide to hydrogen halide which exhaust gases sweep through a dehydration tube, and into the titration cell. Here the amount of halide produced is determined by microcoulometric titration. This is similar to the classical silver/silver chloride potentiometric titration of halide, except silver ions are generated electrolytically at a silver electrode. This technique is more sensitive than the classical silver nitrate titration, as the amount of silver ion generated can be very small yet it can be measured very accurately. Results are quantified as chloride.

Analytical Error and Method Performance

As with all analytical methods, there are measurement errors in AOX analysis. The potential sources of error associated with each operation are listed in Table 1. Errors due to organic chloride contamination or the titration endpoint error are constant in sign and magnitude for all samples, and are unaffected by concentration of AOX in sample. In this text, these errors will be referred to as absolute errors. The magnitude of error resulting from errors in dilution, pipetting, gas leaks, and the inefficiency of generation of Ag^+ ions are proportional to the AOX concentration of the sample. In this text these errors will be referred to as relative errors.

Table 1 Potential sources of error in AOX analytical method.

Operation	**Error**	**Cause or Source of Error**
Sample Adsorption	Organic Chloride Contamination	- contaminated glassware. - contaminated granular activated charcoal. - halide present in chemical reagents and dilution water.
	Measuring Errors	- pipetting and dilution errors in preparation of sample for adsorption.
	Incomplete Adsorption of Sample	- excess amount of dissolved organic material in sample saturating GAC.
Filtration	Organic Chloride Contamination	- contaminated glassware. - contaminated filter membranes. - contaminated air drawn through filter.
TOX Determination	Incomplete Conversion of Organic Halide	- contaminated or pitted surfaces in pyrolysis tube.
	Incomplete Transfer of Hydrogen Halide to the Titration Cell	- leaks at the pyrolysis tube/dehydration tube joint.
	Titration Errors	- inefficient Ag^+ generation due to spent electrolyte or a contaminated generator electrode. - titration end point error.

The errors associated with the method can be further divided into two other separate components: a systematic component which remains constant, and can include both absolute and relative error; and a random component which varies with each determination. The systematic component of error effects the accuracy of the analytical method. In AEC Method E128.0 for AOX, blank subtraction and a calibration factor are used to correct results for the systematic component of the absolute and relative error respectively.

Results cannot be corrected for random component of error where the sign and magnitude of this error may vary randomly with each measurement. The analytical results will be randomly scattered around the true value. In most chemical analyses the distribution of these errors approximates the normal distribution, the probability density function being:

$$p(x)=\frac{1}{\sigma\sqrt{2\pi}}e^{\frac{-(x-\mu)}{2\sigma^2}} \tag{1}$$

where p(x) is the probability density function of result x, μ is the true mean, σ is the true standard deviation and σ^2 is the true variance of the underlying population sampled by the test. Given μ and σ the probability (typically 0.95 or 0.99) of a result x falling in a range x_1 to x_2 can be calculated as the integral of equation 1 between x_1 and x_2. Conversely, for any x, a range with a probability of containing μ may be calculated given σ. As the true value of σ is not know, estimates using the standard deviation, s, of the results of repeated analyses ($n \geq 7$) of a dilute sample, and the Student t distribution are used to calculate the range. The width of this range is a measure of the precision or reproducibility of the analysis.

The precision, or standard deviation also defines the minimum reliable result which can be reported using the analysis. The method detection limit (MDL) is the lowest value which can be reported with a 99% confidence that the true value is greater than zero. It is generally calculated as three times the standard deviation of low level analysis (estimated with at least 6 degrees of freedom). In the case of this AOX method, where the MDL defines the sensitivity of the test, it is crucial to minimize method standard deviation and to control it on a daily basis. This is the main purpose of the Quality Assurance / Quality Control (QA/QC) program.

Quality Assurance / Quality Control (QA/QC) Program

There are two major components of this laboratory's QA/QC program: the documentation and use of **good laboratory practices** (GLP); and the daily performance of routine tests monitored by Shewart control charts. Another minor component is the annual review of QA/QC test results.

GLP's are *rigid* procedures designed to minimize error, give a high degree of reproducibility to analysis and ensure the **safe** implementation of the analysis. These procedures are contained in the method or in relevant standard operating procedures. These practices cover procedures such as: maintenance of the instrument and the equipment; preparation of glassware; preparation and handling of standards; and handling of samples.

Specific to this analysis is another element of GLP, the replicate analysis of samples at different dilutions. This test is used to verify that the GAC has not become saturated and its capacity exceeded. Although this replicate analysis does minimize variation, the primary purpose is to validate each analysis.

Five routine daily tests are used to monitor the performance of the analysis. These specific tests were selected because specific test failures also indicate the remedial action to be taken. Results of five tests are used to determine AOX accuracy and precision:

1 Measurement of analytical blanks - used to monitor background (contamination) and background variation.

2 Analysis of calibration solution - used to determine the instrument response factor and the variation in response factor between analyses.

3 Analysis of samples in duplicate - used to monitor the reproducibility or precision of the method. The method variation or standard deviation can also be calculated from the duplicate results.

4 Analysis of samples fortified with 2-chlorobenzoic acid - used to monitor method accuracy.

5. Analysis of QCA/QCB check standards - the analysis of two standards, one 70% of the analytical range and one 20% of the analytical range. The sum of the two results is used to monitor the calibration intercept and the difference of the two results is used to monitor the calibration slope.

Shewart control charts are used to monitor the results of these daily tests. A typical Shewart chart is shown in Figure 3. The mean, x, and the standard deviation, s, of quality control (QC) test results are plotted on a daily basis. Warning limits and control limits for test results are established for test results and are drawn as dashed horizontal line on the charts. In our implementation, these limits are set such that the probability of a result falling beyond the warning limit is <0.05 and of falling beyond the control limit is <0.01. Results which lie outside these limits indicate that the parameter monitored is out of control and remedial action is necessary.

Monitoring of QC test data using Shewart control charts assumes that the population test data are drawn from one homogenous distribution and that it is possible to calculate confidence intervals. If this is not the case it may not be possible to base warning and control limits on confidence intervals. More importantly, the results of the analysis will not be reliable.

The population of test results is expected to be normally distributed although other distributions are possible. When the test results are normally distributed the distribution of the daily test variances is related to the χ^2 distribution by the equality:

$$s^2=\frac{\chi^2\sigma^2}{(n-1)} \tag{2}$$

where σ^2 is the true variance of the underlying population sampled by the test, s^2 is the observed variance, n is the number of tests, and n-1 is the number of degrees of freedom. The probability frequency function of the χ^2 distribution is:

$$p(x)=\frac{1}{2^{(n-1)}\Gamma\frac{(n-1)}{2}}x^{(\frac{n-1}{2})-1}e^{\frac{-x}{2}} \tag{3}$$

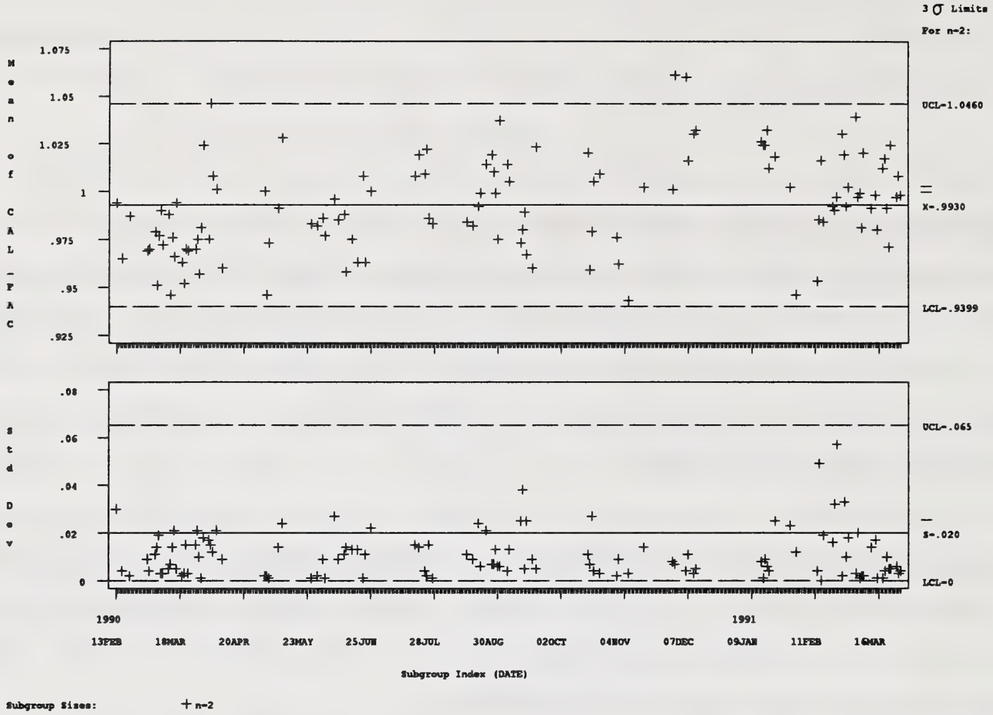

Figure 3 Shewart control chart of calibration factors.

where the only variable is the number of degrees of freedom (*n*-1). When test results are normally distributed, F distribution tables may be used to calculate warning and control limits for variance and/or standard deviation.

Materials and Methods

AOX Quality Control Data

A Mitsubishi TOX-10 organic halide analyzer was used for all AOX measurements. AEC Method E128.O and the equipment and materials specified therein were used for all AOX quality control tests. Quality control data were generated between February, 1990 and April, 1991 (see Appendix 1).

Analysis of Quality Control Data

Analyses of data were done using PC/SAS®[c] ver. 6.04 run on a Fujikama 386 personal computer with a math coprocessor. Outliers in the AOX control data, listed in Appendix 1, were removed based on a 99% confidence interval prior to any analysis.

PROC CAPABILITY procedure of SAS/QC® was used to fit distributions to QC data sets. This software uses a maximin likelihood fitting algorithm[6] and tests the fit using the χ^2 goodness of fit test.[7] Standard test data were fit to normal distributions and the variances of daily tests were fit to γ distributions constrained to χ^2 type distributions with the appropriate number of degrees of freedom. Spearman and Pearson correlations and probabilities between data sets were calculated using the PROC CORR procedure of base SAS®. SAS® source code used is listed in Appendix 2. The results are listed in Appendix 3.

Results and Discussion

The complete set of QC results generated between February 1990 and April 1991 are presented in Appendix 1. These results were evaluated as they were generated using Shewart control charts, as part of the laboratory's QA/QC program. The analysis presented here deals with the distribution of the populations of the results. Distributions fitted to the QC data are summarized in Table 2. The μ and σ of the fitted normal distributions and estimated means and standard deviations of χ^2 type distributions are listed along with probabilities for χ^2 goodness of fit tests and Shapiro Wilk W tests.[7,8]

The Shapiro Wilk W test is used to test if a set of data is normally distributed; it does not test the specific distribution with μ and σ specified. The null hypothesis of the test is "the data are sampled from a normal distribution", and it is rejected with a probability of 0.05 or lower, there being a low probability of falsely rejecting the null hypothesis (95% confidence level). The χ^2 test is used to test the specific fitted distribution. The null hypothesis, being "the fitted distribution is the distribution of the data", is rejected approximate the distribution tested. The fits of data using other distributions were only tested with the χ^2 test as the Shapiro Wilk W test is not applicable to non-normal distributions. All test results were fit to normal distributions and test variances were fit to γ distributions constrained to a χ^2 type distribution with n-1 degrees of freedom. These fitted distributions differ from χ^2 distributions only in scale. They have been rescaled so that the distribution mean is the variance (s^2), rather than the number of degrees of freedom.

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[c] Registered trade mark of SAS Institute Inc.

Calibration Factor

The frequency distributions of calibration factors and the variance of calibration measurements distribution are shown in Figures 4 and 5 respectively. The calibration factors are normally distributed, as is indicated in Figure 4 and by the probabilities of the Shapiro Wilk test and the χ^2 goodness of fit test in Table 2. The variance of calibration factor measurements follow a χ^2 type distribution (1 degree of freedom), shown in Figure 5, and by the probabilities of the χ^2 goodness of fit test. This indicates calibration factor measurement is a random variable, distributed about a true value μ, with a true variance σ^2. The variance can be estimated with s^2, the mean of estimated mean variance data. This variance however is significantly less than that observed for the calibration factor data.

The variance of measurement is constant over time. The two sources of random error contribute to this measurement variance are: the measuring error of the addition of calibration solution with *via* micro syringe; and error in the instruments determination of the added calibrant. We believe the former to be responsible for over half of the variance of these measurements.

The larger variance of the calibration factor data comprises this measurement variance and variance from other sources. The contribution of the measurement variance is small. The variance in the daily estimate of the calibration factor is the variance of the measurement divided by 2, as the estimate is the average of two measurements. From the variances in Table 2 it can be seen that the variance in measurement accounts for approximately 15% of the variance in the distribution of calibration factors (the square of the calibration factor standard deviation).

Table 2 Results of the fits of test results and variances to statistical distributions.

Test Parameter	**Distribution**	***n***	**μ**	**σ**	**Estimated Mean**	**Estimated Std. Dev.**	**χ^2: Prob.**	**Shapiro W: Prob.**
Calibration Factor	Normal	118	0.993	0.025			0.476	0.205
Calibration Factor Variation	Constrained γ	118			0.0001735		0.305	
Method Blank	Normal	116	0.429	0.111			0.002	0.043
	Log Normal				0.429	0.115	0.008	
	γ				0.428	0.111	0.015	
Method Blank Variation	Constrained γ	118			0.006574		0.289	
Recovery of 2-Chlorobenzoic Acid	Normal	77	98.62	3.57			0.647	0.925
Squared Differences of Duplicate Analyses								
< 5 μg Range	Constrained γ	64			0.05386		0.399	
5 to < 15 μg Range	Constrained γ	30			0.10887	0.358		
QCA + QCB	Normal	33	39.18	1.23			0.557	0.858
QCA - QCB	Normal	33	19.91	1.00			0.047	0.027

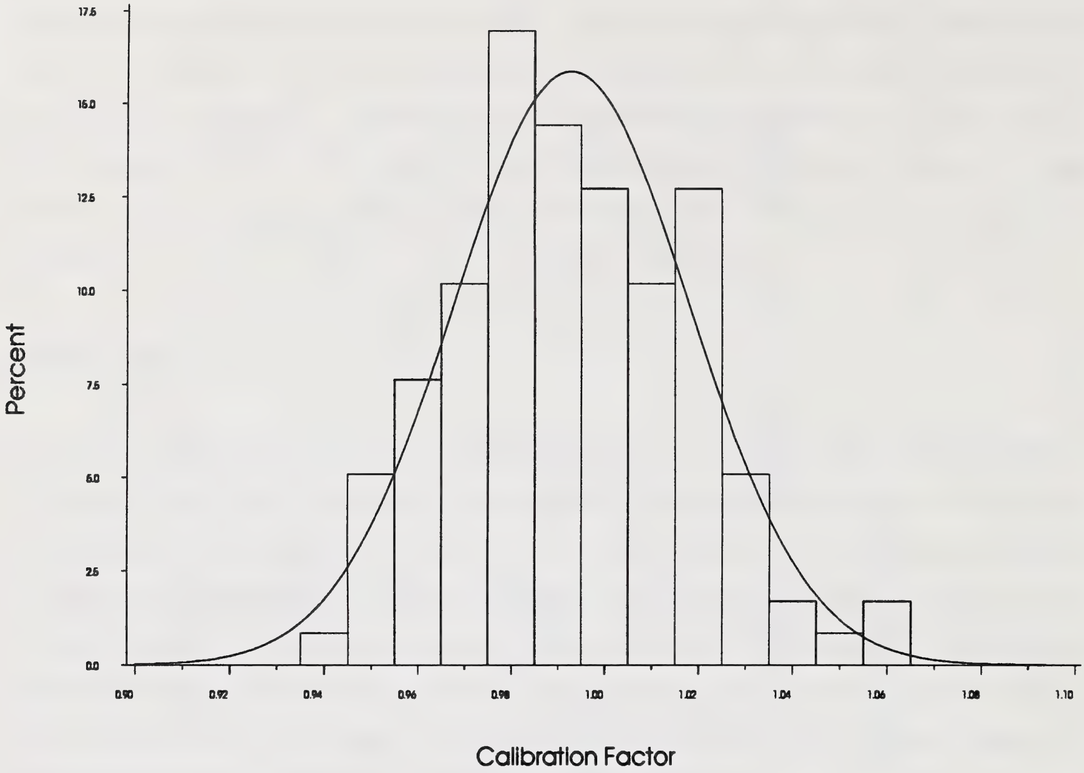

Figure 4 Calibration factor distribution and fitted normal distribution.

Furthermore, the variance of measurement is independent of the daily estimate of the calibration factor. Figure 6 is a scatter plot of the data ranks of the calibration factor vs the rank of the variance of measurement of calibration factor data sets. They appear to be uncorrelated. This is supported by the Spearman rank correlation coefficient of –0.035 for the two data sets which does not differ significantly from zero (probability ≥ 0.702).

While the true variance of the measurement of the calibration factors is constant and independent of the calibration factor, the true value of the calibration factor is a normal random variable changing on a day to day basis, with its own variance, 7 times that of the measurement variance. These daily changes are the result of the small changes in instrument performance which accompany the daily instrument maintenance, startup and shutdown. This has important implications in the interpretation of QC results

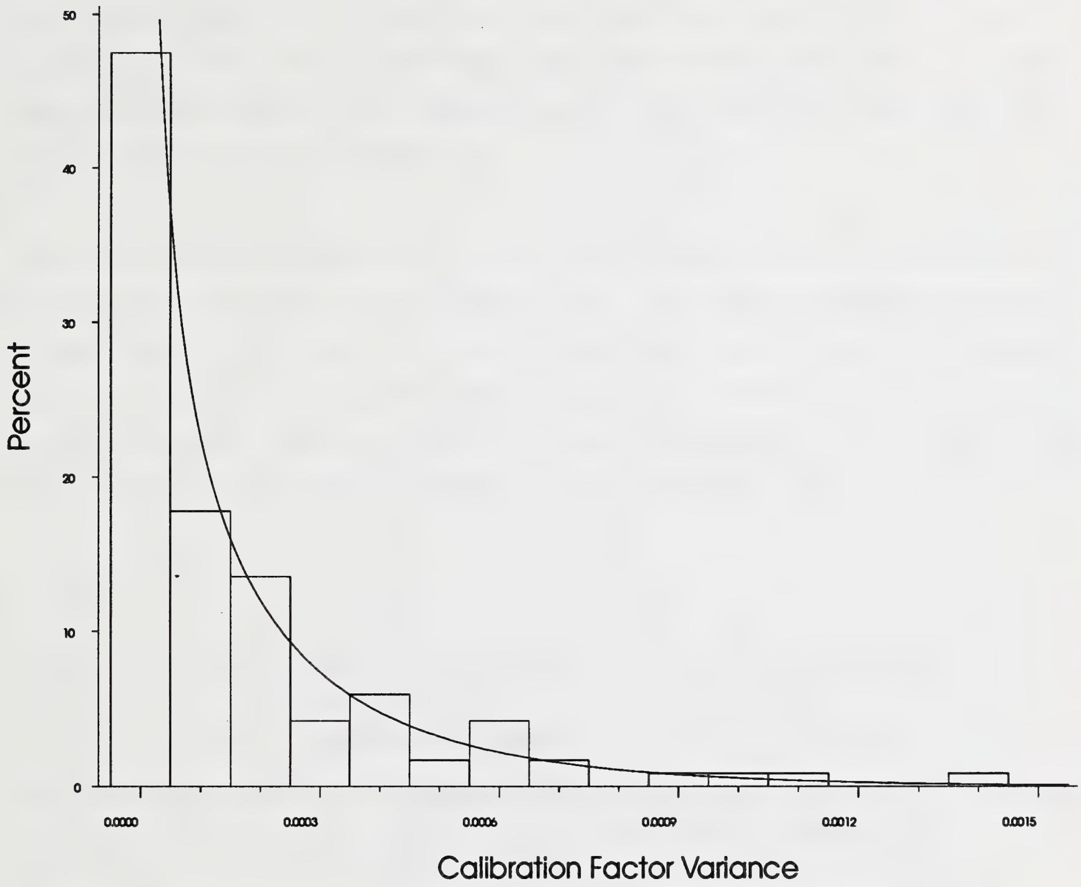

Figure 5 Distribution of variance of calibration factor measurement variance and fitted χ^2 type distribution (1 degree of freedom).

and their use in the optimization of method performance.

The variance in the measurement of the calibration factor is the variance of instrumental determination of halide and hence is part of the variation in the measurement of AOX. It is very important to monitor and control this variation. The random daily changes in calibration factor do not affect the results generated by the method as they are compensated for in the calculation of AOX.

The calibration factor is a much less precise parameter to control the analysis with but can be used to judge the state of the instrument and to determine when maintenance is necessary. Tight control limits

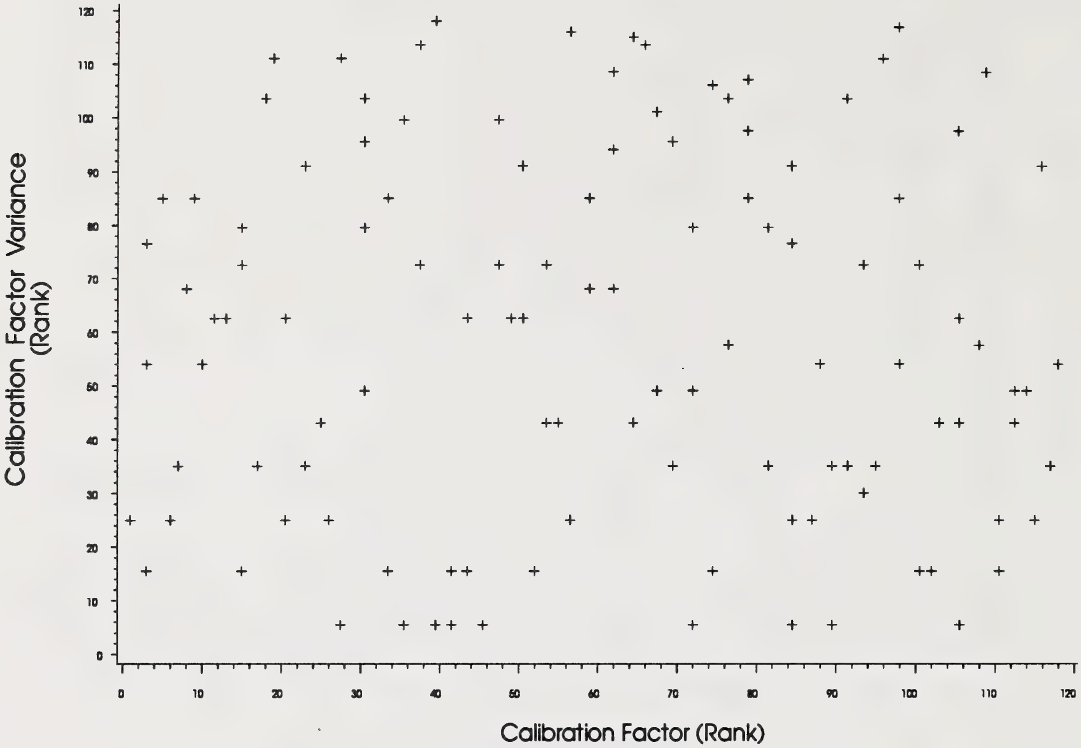

Figure 6 Scatter plot of rank of the variance of the calibration factor measurement versus the rank of measured calibration factor.

are not necessary for this parameter, and could result in needless shut downs. For this reason calibration factor control limits specified in AEC Method E128.0, 0.95 and 1.05, should be relaxed for normal operations.

Method Blanks

The distribution of the method blank data and the variance of method blank determination are shown in Figures 7 and 8. The Shapiro Wilk W and the χ^2 goodness of fit test probabilities indicate that, unlike the calibration factor data, the method blank data do not conform to a normal distribution, a log normal distribution, or a γ distribution. This is not surprising as the method blank is the one QC test influenced by factors beyond the control of the laboratory. Sources of contamination such as laboratory reagents, GAC, and polycarbonate filters are tested to meet method specifications; rigorous glassware preparation procedures are specified; but the contamination through building services, such as the air recirculation system and laboratory water are not completely in control of the laboratory. It is these services which cause nonrandom changes in the method blank.

The variance of the daily measurements of the blank conforms to a χ^2 type distribution, indicating that the daily estimate of the blank is a normal random variable. The variance of the daily measurement of the blank, however, is independent of the true daily blank, itself a random variable, as is illustrated in Figure 9, a scatter plot of the data ranks of the blank and the blank variance data sets. They appear to be entirely independent. This is supported by the Spearman rank correlation of -0.128 for the two data sets which does not differ significantly from zero (probability ≥ 0.167).

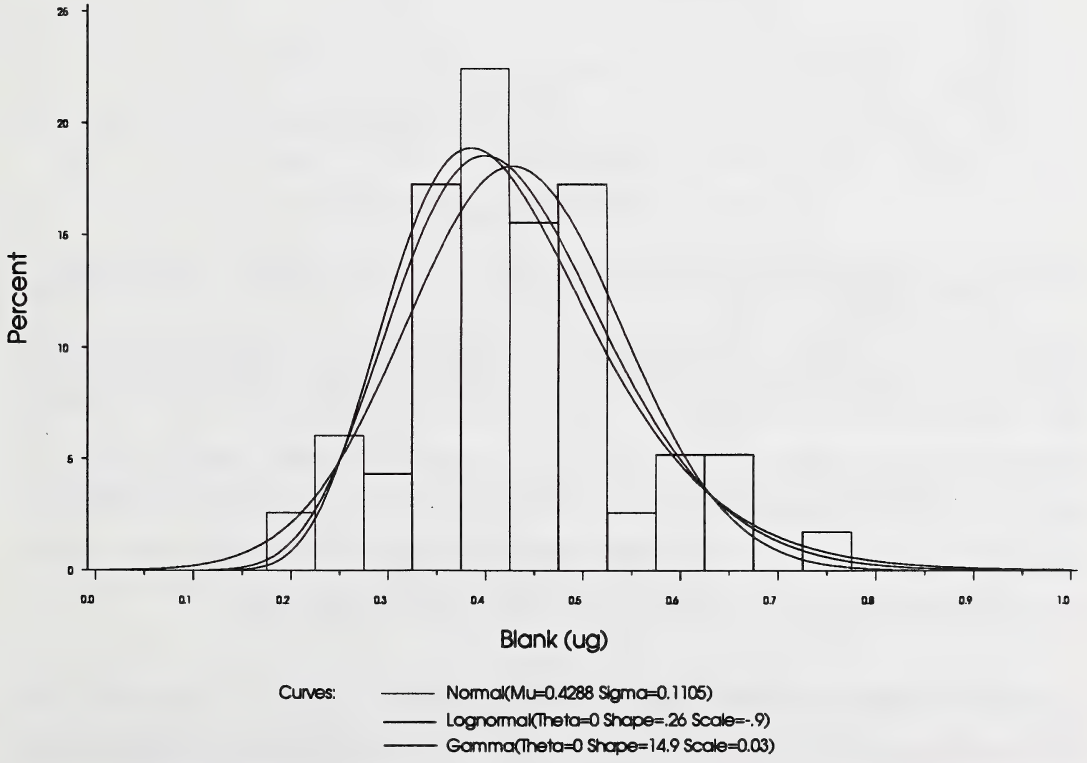

Figure 7 Distribution of method blanks and fitted normal, lognormal and γ distributions.

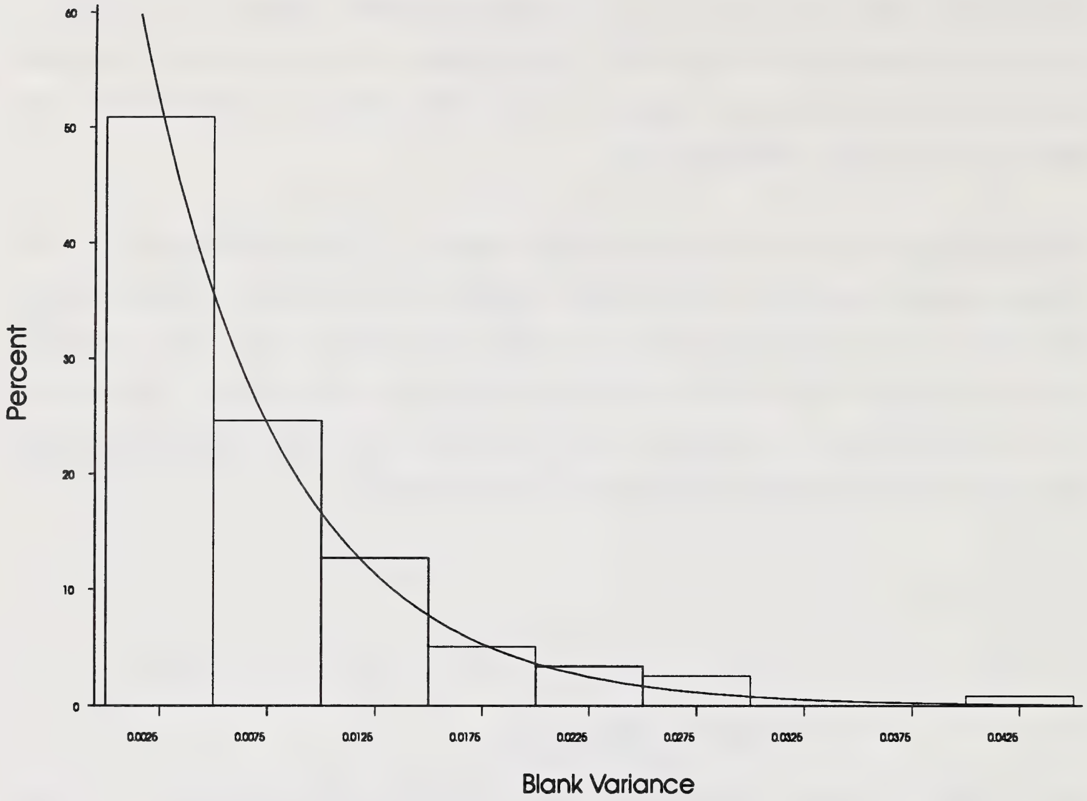

Figure 8 Distribution of method blank measurement variation and fitted χ^2 type distribution (2 degrees of freedom).

This independence of the two data sets is very important because it demonstrates that the variance in the blank measurement is not influenced by the factors affecting blank value. This means that although method performance is affected by the variance of the measurement of method blank, the effect of the method blank itself is negligible with in the range encountered. Rigorous control of the method blank is not necessary and control limits may be relaxed. Improvements in the source laboratory water used have now been made and these may be reflected in the distribution of future QC data.

Estimation of Method Variance and Method Standard Deviation

The results of the duplicate analysis of samples are used to estimate the variance and standard deviation of the method. In this discussion the only results of samples which responded in the low range of the

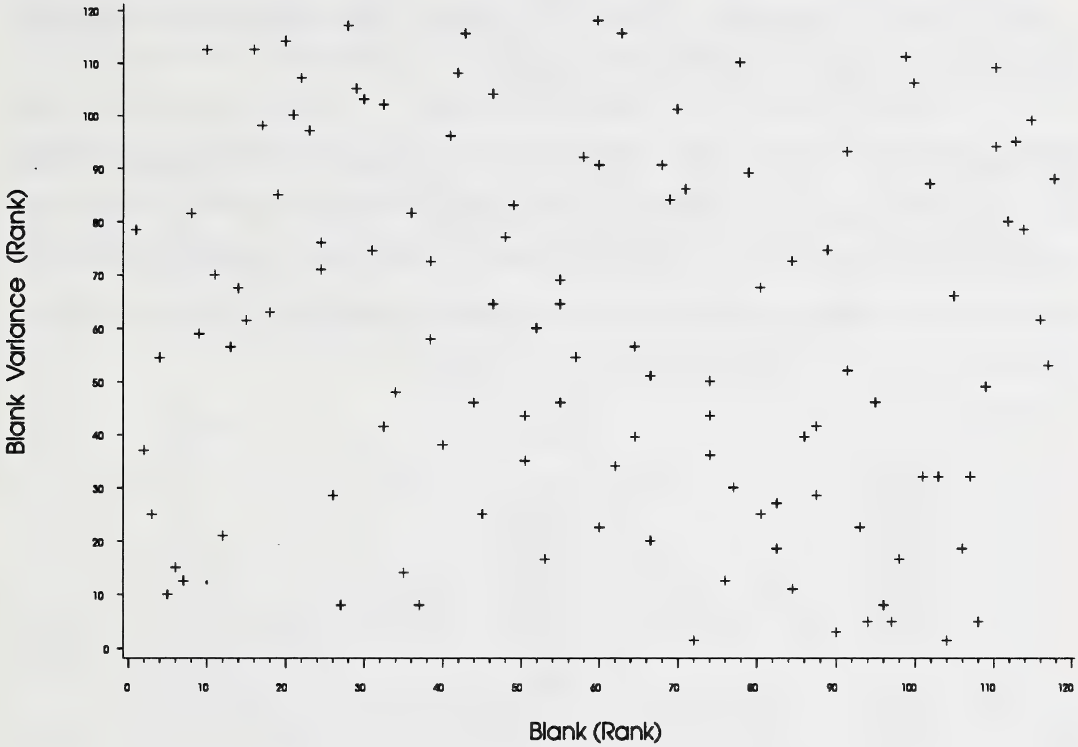

Figure 9 Scatter plot of rank of blank variance versus rank of blank.

organic halide analyzer (< 5 µg as chloride) are considered as the standard deviation at low concentrations is used to calculate the MDL. The results of duplicate analysis of more concentrated samples have also been analyzed (Table 2) and the relative differences are less than those found in low concentration samples

The variance is estimated from the square of the differences of duplicate analysis using the equation:

$$s^2=2\times\left(\frac{\Delta AOX}{2}\right)^2=\frac{\Delta AOX^2}{2} \tag{4}$$

which was obtained by substituting ΔAOX, the difference in the instrument responses of the two analyses, into the equation for the standard deviation of a normally distributed set of data. Figure 10 shows the distribution of the square of the differences in duplicate analysis of low response samples. These data conform to a χ^2 type distribution, the probability of a greater χ^2 value being 0.399, thus indicating a satisfactory fit of the parameters in Table 2, to the data.

The estimate of AOX method variance of the method is mean of the square of the duplicate differences divided by 2. The method standard deviation can be estimated as the square root of this estimate of the method variance, $(0.0586/2)^{0.5} = 0.17$ µg halide as chloride. This estimates the method standard deviation in terms of chloride detected. Division 0.1 L converts the method standard deviation to concentration for undiluted low concentration samples, 1.7 µg/L or 0.0017 mg/L.

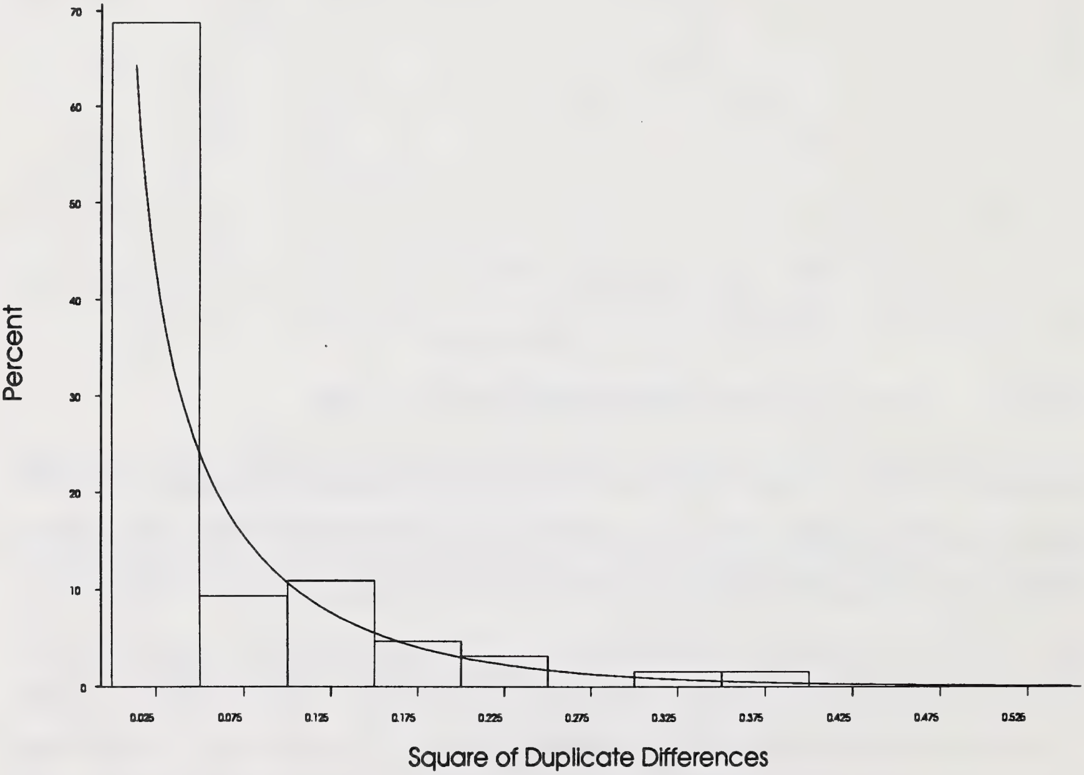

Figure 10 Distribution of squares of duplicate differences (low range) and fitted χ^2 type distribution (1 degree of freedom).

The method standard deviation for low concentration samples can also be estimated from the set of results from repeated analysis of low concentration samples. Two such sets of results are listed in Table 3. The two estimates of the method standard deviation, 0.0013 and 0.0017 mg/L, do not differ significantly($p >$ 0.25), nor do they differ significantly ($p > 0.25$) from the method standard deviation estimated from the differences in duplicate analysis. The distribution of the square of the differences also indicates that the standard deviation remains constant over time and that these estimates of method standard deviation apply to all data generated in our laboratory with this method in control. The MDL of this method in our laboratory is 0.005 mg/L and is applicable to undiluted Alberta river water receiving treated BKME.

Table 3 Results of replicate analysis of low concentration river samples.

Determination	**Site #1** **µg Cl**	**Site #2** **µg Cl**
1	0.0266	0.0049
2	0.0269	0.0079
3	0.0253	0.0085
4	0.0258	0.0048
5	0.0255	0.0078
6	0.0238	0.0072
7	0.0280	0.0061
8	0.0267	0.0038
9		0.0052
Average	0.0261	0.0062
Standard Deviation	0.0013	0.0017

It is inappropriate to apply this estimate of the MDL to BKME. In BKME the concentration of organic material and AOX is far higher than that found in river waters. Dilution of the sample is necessary to avoid saturation of the GAC, and/or overloading the instrument with chloride. The MDL, or standard deviation of the method, must be adjusted to take into account the dilution used. In samples with high concentrations of organic material and low concentrations of AOX, such as chemi-thermomechanical pulp (CTMP) mill effluents, the dilutions required to avoid the saturation of the GAC may make it impossible to observe any AOX.

The detection and measurement of AOX by this method is also affected by the criteria for the agreement, within 10%, of replicate analyses. In river samples, with AOX concentrations below 0.020 µg/L, the replicate criteria is difficult of fulfill although the GAC does not become saturated. The replicate criteria is based on a relative difference which can exceed the absolute method error at these low concentrations. In such samples the replicate criteria may lead to the rejection of useful data.

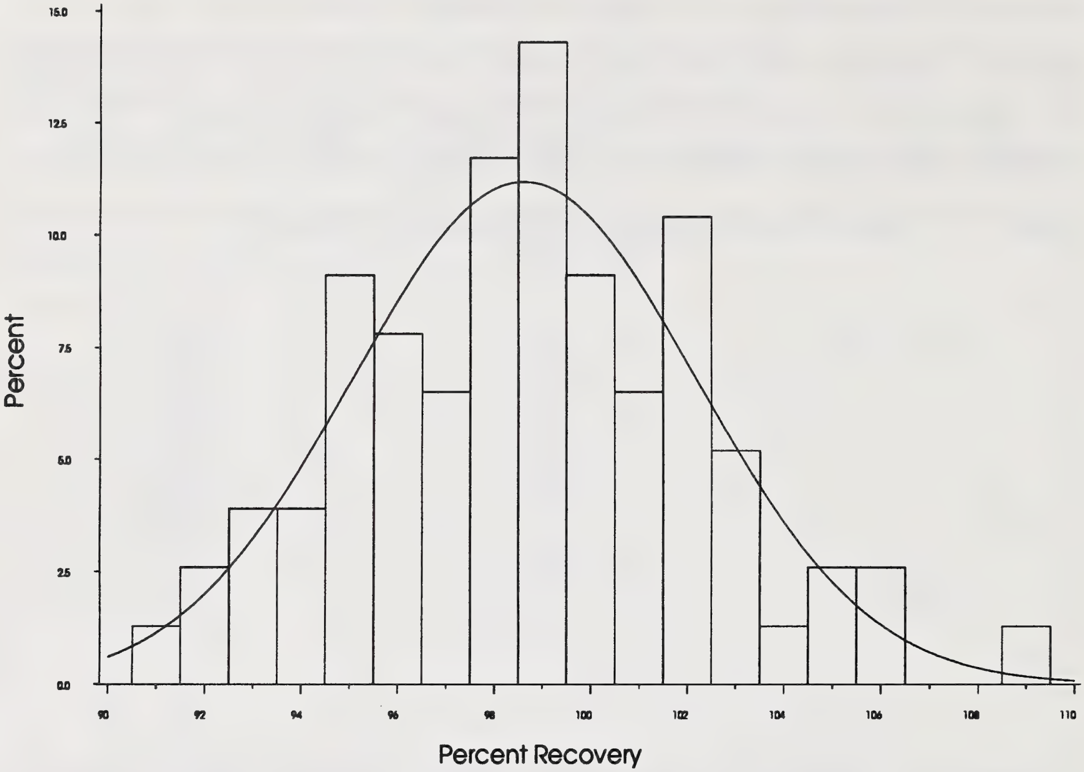

Figure 11 Distribution of the recovery of 2-chlorobenzoic acid from fortified samples and fitted normal distribution.

Recovery of 2-Chlorobenzoic Acid

The distribution of 2-chlorobenzoic acid recoveries is shown in Figure 11. This test is based on the recovery of 10 μg chloride added, as 2-chlorobenzoic acid, to samples. The recovery will be influenced by: systematic errors due to calibration; a high variation in the blank; or poor sample adsorption.

The data are normally distributed with probabilities of 0.925 for a greater Shapiro Wilk W test statistic and 0.647 for the χ^2 goodness of fit test of the fitted distribution (Table 2). The mean recovery of 98.62%

indicates almost quantitative recovery of the spiked acid. The standard deviation of 3.57% indicates an approximate standard deviation of 0.36 µg (based on a 10 µg determination) which is considerably higher than the estimates of the method standard deviation in the preceding section. This is due to a number of factors: method results are based on the average of two replicate analysis, not one determination as with the spiked sample; the recovery is calculated using the difference of analyses, which increases the random error; the recovery contains random error associated with the addition of the 2-chlorobenzoic acid to the sample; and the instrument range used in the analysis of the spiked sample is > 10 µg where the absolute error is higher than the error in the low concentration data used above to estimate the method standard deviation.

The recovery then is not a particularly sensitive QC test but, as failures in this test should be accompanied by the failure of another QC test, it can be used to confirm other test failures, to discriminate between random events or real changes in the test. It may also be used to determine if the GAC is saturated in the analysis of low AOX concentration where the replicate criteria is not met.

QCA/QCB Calibration Check Standards

The QCA/QCB test is used to evaluate the instrument calibration. Two measurements of standard solutions, one at 70% of the instrument range (QCA), and one at 20% of the instrument range (QCB) are made. The measurements are corrected for calibration and the sum and difference are used to evaluate the slope and intercept of the calibration respectively (note in this method the zero is always used as the intercept). The analysis and discussion of this test data presented here is only preliminary as the data set contains only 33 points. The distributions of the sum and difference data sets, along with the probabilities of the Shapiro Wilk W test and the χ^2 test of fit, are listed in Table 2.

The test results in Table 2 indicate that the distribution of the sum data is normal but that the difference of the difference data differs significantly from normality. However, as this discussion is preliminary and involves a small data set, the difference data will be treated as normally distributed to simplify the analysis.

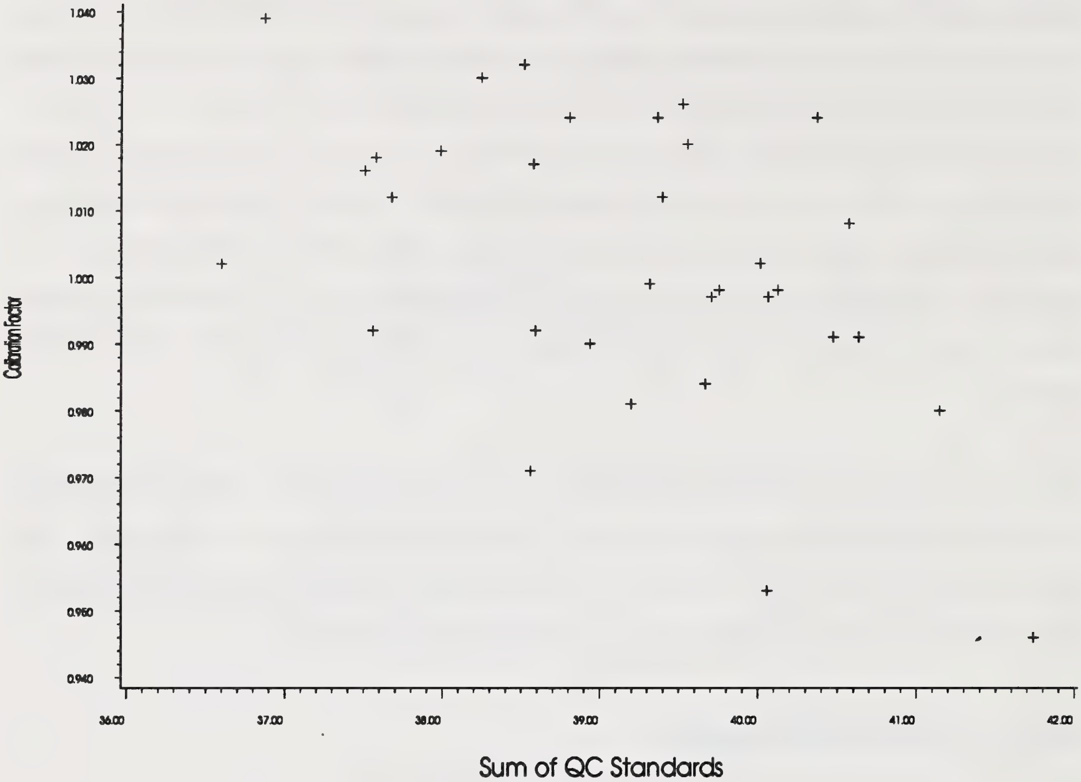

Figure 12 Scatter plot of calibration factor and QCA/QCB sum parameter.

The standard deviation of the sum data is 1.23 µg chloride, which although not unreasonable as it contains the errors of a mid range (5 to 15 µg chloride) and a high range measurement (greater than 15 µg chloride), suggests that this test may not be precise enough for tight control of the calibration factor. Figure 12 shows the scatter plot of the calibration factor versus the sum data. A negative correlation between the two sets of data is obvious. The Pearson correlation of -0.487 between the sets of data is significantly different from 0 at $P \leq 0.004$. It is apparent the that this test is sensitive to errors in the estimation of the calibration factor although a simple Shewart chart of the data may not be an effective method to analyze the daily results. Analysis using a scatter plot, or a Shewart chart of a function of the calibration factor and the sum result, may prove to be more effective in detecting outliers. This will be investigated further as more data become available.

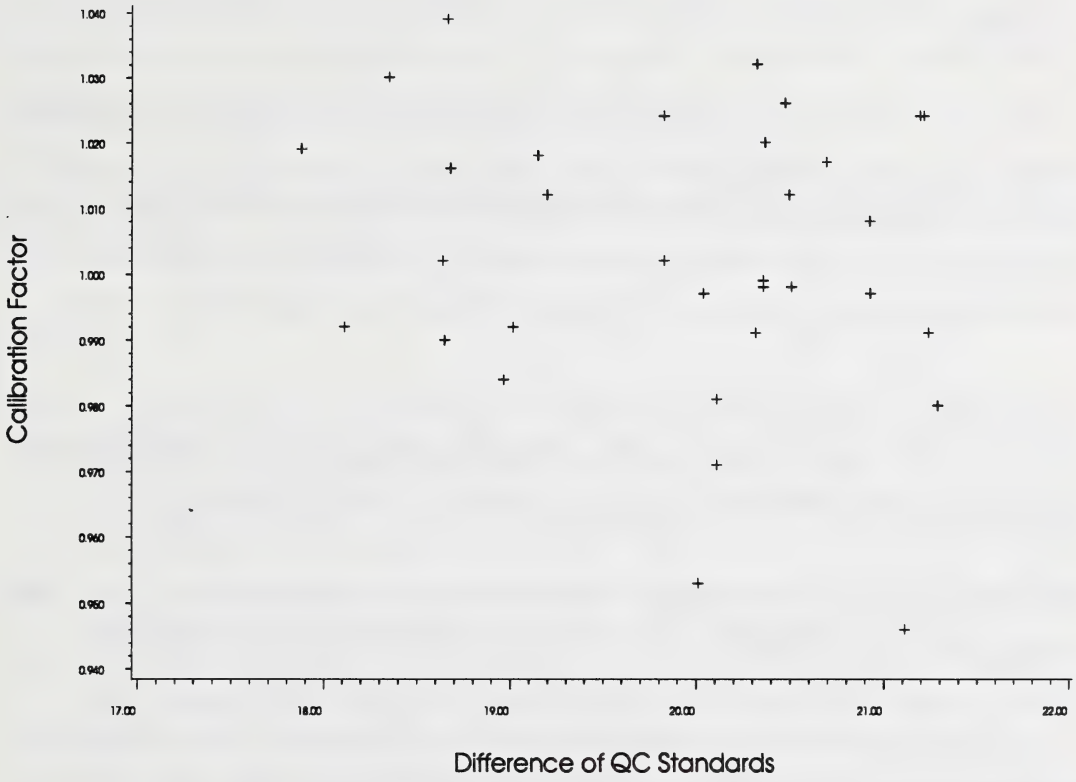

Figure 13 Scatter plot of calibration factor and QCA/QCB difference parameter.

The scatter plot of the calibration factor and the difference data is shown in Figure 13. The two data sets are not correlated; the Pearson correlation coefficient (-0.189) does not differ significantly different than zero (probability ≥ 0.293). This is not unexpected as the difference between QCA and QCB is meant to be used to control the intercept and should have a very low correlation the slope of the calibration. The standard deviation in the difference data is 1.00 µg, suggesting that it has little value in controlling the calibration intercept.

As part of the instrument operating procedure, the instrument is cycled repeatedly at startup with no sample, until the chloride is detected at less than 0.05 µg. Under normal conditions the instrument blank remains relatively constant and the calibration intercept is treated as zero. However, data will continue to be collected so that the effectiveness of the test may be analyzed more rigorously.

Conclusions

1. The method standard deviation of this analysis is approximately 0.0017 mg/L AOX as chloride for undiluted river waters receiving pulp and paper effluents and the true MDL for these samples is approximately 0.005 mg/L AOX as chloride. The method standard deviation for BKME samples is 0.0023 mg/L (based on the mid range replicate differences) adjusted for the dilution used in the analysis. This results in a method standard deviation of 0.23 mg/L for BKME samples diluted 1.0 mL to 100 mL.

2. The calibration factor and blank control limits may be relaxed with little or no impact on method performance. The variance of the measurement of these parameters, which effect method performance and are independent of the measurements, must be monitored and controlled rigorously.

3. All QC test results, with the exception of the method blank, are either normal or χ^2 type random variates, therefore the probabilities used in the calculation of control limits are true probabilities.

4. The QCA/QCB sum parameter is significantly correlated with the calibration factor and although there is considerable random error in the parameter, it may be possible to use it in conjunction with the calibration factor to effectively control the calibration factor. The QCA/QCB difference parameter appears to contain too much random error to be useful in the control of a calibration intercept.

Revision to be Made to AEC Method E128.0

1. The AEC method E128.0 will be revised to be applicable to receiving waters as well as bleached kraft mill effluents. Accordingly the method has been renamed to AE128.1 to reflect these changes.

2. The stated MDL of method E128.0 for undiluted samples will be lowered to 0.010 mg/L AOX as chloride. The replicate criteria of 10% should only be rigorously applied to samples over 0.020 mg/L AOX as chloride and when not met in less concentrated samples the results may be reported with the failure to meet the replicate criteria noted.

3. The control limits for the calibration factor and the blank should be relaxed to 0.90 to 1.05 for the calibration factor and less than 0.75 for the blank. Data generated using these relaxed limits should be analyzed for any negative impact of these changes on data quality.

4. QCA/QCB data should continue to be collected and the sum and difference parameters should be further evaluated when enough data is available.

References

1. Methods for the Examination of Water and Waste Water: Method 506 Organic Halogen (Dissolved). American Public Health Association, Washington, D.C. (1989)
2. L. Sjöström, R. Rådeström, and K. Lindström; "Determination of Total Organic Chlorine in Spent Bleach Liquors," *Svensk Papperstidning*, **85**(3):R7 (1982).
3. DIN: DIN 38409H 14 Summarische Wirkungs and Stoffkenngro Ben (Gruppe H), Bestimmung der adsobierbaren organisch gebundenen halogen (AOX), Beuth-Verlag, Berlin (1985).
4. L.R. Noton, "Adsorbable Organic Halide (AOX) (Sampling in the Athabasca and Wapiti-Smoky Rivers, Fall and Winter 1989-1990," Alberta Environment, Environmental Assessment Division (1991).
5. C.I. Johnson, L.R. Noton, and R.D. Smillie, "The Fate of AOX in the Athabasca and Wapiti-Smoky Rivers," *in preparation.*
6. N.L. Johnson and S. Kotz, *Continuous Univaraite Distributions - 1*, Boston: Houghten and Mifflin, pg 185-186 (1970).
7. G.W. Sndecor and W.G. Cochran, *Statistica Methods, Seventh Edition*, Ames: The Iowa State University Press, pg 75-78 (1980).
8. S.S. Shapiro and M.B. Wilk; "An Analysis of Variance Test for Normality (Complete Samples)," *Biomerika*, **52**, 591 (1965).

Appendix 1

Quality Control Data from February 1990 to May 1991

Table A1.1

Quality control data from February 1990 to May 1991.

OBS	DATE	BLANK	BK_STD	CAL_FAC	CF_STD	QCAPLUS	QCAMINUS	BK_VAR	CF_VAR
1	15MAR1991	0.582	0.003	0.980	0.001	41.15	21.29	0.000009	0.000001
2	13SEP1990	0.452	0.003	0.989	0.005	38.98	22.67	0.000009	0.000025
3	25MAY1990	0.489	0.004	0.983	0.001	37.31	21.88	0.000016	0.000001
4	21JUN1990	0.616	0.009	1.008	0.001	36.09	20.83	0.000081	0.000001
5	08MAR1991	0.506	0.009	1.020	0.002	39.56	20.37	0.000081	0.000004
6	26MAR1991	0.499	0.009	1.008	0.003	40.58	20.93	0.000081	0.000009
7	06NOV1990	0.377	0.011	0.943	0.003	38.05	22.68	0.000121	0.000009
8	31MAY1990	0.359	0.011	0.986	0.009	36.06	19.99	0.000121	0.000081
9	17SEP1990	0.505	0.011	0.960	0.009	39.18	22.87	0.000121	0.000081
10	01FEB1991	0.241	0.012	0.946	0.012	41.74	21.11	0.000144	0.000144
11	18JAN1991	0.482	0.013	1.012	0.004	37.68	19.20	0.000169	0.000016
12	28AUG1990	0.243	0.015	1.010	0.007	37.48	21.31	0.000225	0.000049
13	02APR1990	0.457	0.015	0.975	0.017	40.28	22.84	0.000225	0.000289
14	06JUN1990	0.374	0.017	0.996	0.027	37.40	21.92	0.000289	0.000729
15	14MAR1990	0.242	0.021	0.976	0.014	37.48	22.12	0.000441	0.000196
16	21MAR1990	0.398	0.022	0.970	0.015	38.58	22.90	0.000484	0.000225
17	15FEB1991	0.518	0.022	0.984	0.019	39.67	18.97	0.000484	0.000361
18	19OCT1990	0.600	0.023	1.005	0.004	39.48	23.02	0.000529	0.000016
19	22MAR1991	0.481	0.023	1.024	0.005	40.38	21.20	0.000529	0.000025
20	04MAR1991	0.440	0.024	1.039	0.003	36.87	18.67	0.000576	0.000009
21	01JUN1990	0.296	0.025	0.977	0.001	.	.	0.000625	0.000001
22	29JAN1991	0.497	0.028	1.002	0.023	36.60	18.64	0.000784	0.000529
23	20AUG1990	0.424	0.028	0.992	0.024	37.41	21.79	0.000784	0.000576
24	16MAR1990	0.220	0.030	0.994	0.005	.	.	0.000900	0.000025
25	08JUN1990	0.387	0.030	0.985	0.009	37.85	21.15	0.000900	0.000081
26	12MAR1991	0.475	0.030	0.991	0.014	40.48	20.32	0.000900	0.000196
27	18MAR1991	0.481	0.031	1.012	0.001	39.40	20.50	0.000961	0.000001
28	30NOV1990	0.357	0.032	1.061	0.007	36.15	22.19	0.001024	0.000049
29	27FEB1991	0.486	0.032	0.992	0.010	38.59	19.02	0.001024	0.000100
30	25MAR1991	0.466	0.033	0.997	0.006	40.07	20.93	0.001089	0.000036
31	31OCT1990	0.559	0.034	0.976	0.002	41.04	23.87	0.001156	0.000004
32	16JAN1991	0.577	0.034	1.024	0.009	38.81	19.83	0.001156	0.000081
33	21FEB1991	0.615	0.034	0.990	0.032	38.94	18.65	0.001156	0.001024
34	20MAR1990	0.435	0.035	0.952	0.003	40.57	25.20	0.001225	0.000009
35	30AUG1990	0.392	0.036	0.975	0.006	38.13	22.22	0.001296	0.000036
36	19MAR1991	0.453	0.037	1.017	0.004	38.58	20.70	0.001369	0.000016
37	16FEB1990	0.210	0.038	0.965	0.004	41.10	24.35	0.001444	0.000016
38	11DEC1990	0.380	0.039	1.032	0.005	38.84	22.95	0.001521	0.000025
39	06MAR1991	0.483	0.040	0.999	0.001	39.32	20.36	0.001600	0.000001
40	29NOV1990	0.438	0.040	1.001	0.008	39.08	23.70	0.001600	0.000064
41	02MAY1990	0.367	0.043	0.946	0.002	38.54	22.39	0.001849	0.000004
42	21MAR1991	0.486	0.043	0.971	0.005	38.56	20.11	0.001849	0.000025
43	20MAR1991	0.453	0.045	0.991	0.010	40.64	21.24	0.002025	0.000100
44	14SEP1990	0.392	0.045	0.967	0.025	37.57	22.40	0.002025	0.000625
45	01MAR1990	0.386	0.046	0.969	0.009	.	.	0.002116	0.000081
46	14MAR1991	0.502	0.046	0.998	0.017	39.76	20.36	0.002116	0.000289
47	13FEB1990	0.402	0.046	0.994	0.030	.	.	0.002116	0.000900
48	11JUN1990	0.373	0.047	0.988	0.011	38.37	23.03	0.002209	0.000121
49	12FEB1991	0.625	0.048	0.953	0.004	40.06	20.01	0.002304	0.000016
50	25FEB1991	0.453	0.050	1.030	0.002	38.25	18.35	0.002500	0.000004
51	26MAR1990	0.440	0.053	0.970	0.015	37.26	22.71	0.002809	0.000225
52	17JAN1991	0.495	0.054	1.032	0.006	38.52	20.33	0.002916	0.000036
53	18JUN1990	0.857	0.056	0.963	0.013	38.56	22.73	0.003136	0.000169
54	06DEC1990	0.235	0.063	1.060	0.004	34.77	18.88	0.003969	0.000016
55	27MAR1990	0.403	0.063	0.975	0.021	35.71	20.80	0.003969	0.000441
56	04SEP1990	0.438	0.065	1.014	0.004	37.12	20.84	0.004225	0.000016
57	25JUL1990	0.314	0.065	0.986	0.015	36.50	22.27	0.004225	0.000225
58	01MAY1990	0.379	0.066	1.000	0.002	39.13	23.24	0.004356	0.000004
59	28MAY1990	0.267	0.069	0.982	0.002	36.98	23.63	0.004761	0.000004
60	31AUG1990	0.394	0.070	1.037	0.006	36.45	20.75	0.004900	0.000036
61	15JAN1991	0.755	0.071	1.024	0.001	39.37	21.22	0.005041	0.000001
62	07DEC1990	0.322	0.071	1.016	0.011	40.18	23.72	0.005041	0.000121
63	14NOV1990	0.328	0.072	1.002	0.014	36.64	22.49	0.005184	0.000196
64	21AUG1990	0.388	0.073	0.999	0.006	37.35	21.63	0.005329	0.000036
65	05SEP1990	0.402	0.073	1.005	0.013	38.25	21.92	0.005329	0.000169
66	14JAN1991	0.587	0.074	1.026	0.008	39.53	20.48	0.005476	0.000064
67	10DEC1990	0.475	0.075	1.030	0.003	40.23	23.90	0.005625	0.000009
68	15MAR1990	0.320	0.075	0.966	0.021	37.23	21.94	0.005625	0.000441
69	09MAR1990	0.402	0.076	0.972	0.003	37.87	20.71	0.005776	0.000009
70	10MAY1990	0.277	0.077	1.028	0.024	35.61	20.55	0.005929	0.000576
71	06APR1990	0.355	0.079	1.001	0.021	36.65	21.75	0.006241	0.000441
72	27MAR1991	0.482	0.081	0.998	0.004	40.13	20.51	0.006561	0.000016
73	12MAR1990	0.379	0.081	0.988	0.005	36.20	21.48	0.006561	0.000025
74	30MAR1990	0.366	0.083	1.024	0.018	37.24	21.65	0.006889	0.000324

Table A1.1 (continued)

Quality control data from February 1990 to May 1991.

OBS	DATE	BLANK	BK_STD	CAL_FAC	CF_STD	QCAPLUS	QCAMINUS	BK_VAR	CF_VAR
75	11SEP1990	0.488	0.083	0.973	0.025	39.63	23.52	0.006889	0.000625
76	20JUL1990	0.355	0.084	1.019	0.014	38.13	21.87	0.007056	0.000196
77	05MAR1990	0.390	0.085	0.979	0.011	37.41	21.20	0.007225	0.000121
78	07MAR1990	0.191	0.086	0.977	0.019	37.02	21.18	0.007396	0.000361
79	21JAN1991	0.658	0.086	1.018	0.025	37.58	19.15	0.007396	0.000625
80	18JUL1990	0.647	0.087	1.008	0.015	38.20	21.53	0.007569	0.000225
81	27JUL1990	0.250	0.089	0.983	0.001	38.16	22.67	0.007921	0.000001
82	13MAR1990	0.376	0.089	0.946	0.007	37.38	20.94	0.007921	0.000049
83	28FEB1991	0.391	0.090	1.002	0.018	40.02	19.83	0.008100	0.000324
84	22OCT1990	0.447	0.091	1.009	0.003	39.76	24.12	0.008281	0.000009
85	29MAR1990	0.330	0.093	0.981	0.001	.	.	0.008649	0.000001
86	20FEB1991	0.451	0.094	0.992	0.016	37.56	18.11	0.008836	0.000256
87	24AUG1990	0.570	0.097	1.014	0.021	37.14	21.25	0.009409	0.000441
88	15JUN1990	0.993	0.098	0.975	0.013	37.16	20.91	0.009604	0.000169
89	16OCT1990	0.471	0.099	1.020	0.011	36.27	19.40	0.009801	0.000121
90	19SEP1990	0.424	0.100	1.023	0.005	36.09	20.64	0.010000	0.000025
91	27AUG1990	0.442	0.100	1.019	0.007	37.50	21.32	0.010000	0.000049
92	20FEB1990	0.404	0.102	0.987	0.002	40.18	22.10	0.010404	0.000004
93	26FEB1991	0.495	0.103	1.019	0.033	37.99	17.88	0.010609	0.001089
94	25JUN1990	0.644	0.104	1.000	0.022	36.80	21.49	0.010816	0.000484
95	12SEP1990	0.649	0.106	0.980	0.038	39.39	22.20	0.011236	0.001444
96	03MAY1990	0.381	0.107	0.973	0.001	36.74	20.84	0.011449	0.000001
97	02MAR1990	0.351	0.109	0.970	0.004	37.41	22.57	0.011881	0.000016
98	08MAR1990	0.326	0.111	0.990	0.003	36.56	21.29	0.012321	0.000009
99	14AUG1990	0.737	0.112	0.984	0.011	37.99	21.72	0.012544	0.000121
100	17AUG1990	0.344	0.114	0.982	0.009	38.53	21.88	0.012996	0.000081
101	28MAR1990	0.450	0.115	0.957	0.010	38.03	20.13	0.013225	0.000100
102	03APR1990	0.367	0.116	1.046	0.015	35.09	20.71	0.013456	0.000225
103	18OCT1990	0.365	0.120	0.979	0.027	39.51	23.27	0.014400	0.000729
104	19MAR1990	0.388	0.122	0.963	0.002	38.81	20.53	0.014884	0.000004
105	22MAR1990	0.364	0.124	0.969	0.003	36.23	21.02	0.015376	0.000009
106	14FEB1991	0.550	0.125	1.016	0.000	37.51	18.68	0.015625	0.000010
107	01NOV1990	0.348	0.126	0.962	0.009	37.69	21.71	0.015876	0.000081
108	06MAR1990	0.383	0.131	0.951	0.014	38.02	20.77	0.017161	0.000196
109	17OCT1990	0.644	0.134	0.959	0.007	40.68	25.15	0.017956	0.000049
110	05MAR1991	0.470	0.139	0.997	0.020	39.71	20.04	0.019321	0.000400
111	07MAR1991	0.522	0.143	0.981	0.002	39.20	20.11	0.020449	0.000004
112	22JUN1990	0.325	0.145	0.963	0.011	39.11	21.77	0.021025	0.000121
113	08MAY1990	0.269	0.145	0.991	0.014	37.02	21.18	0.021025	0.000196
114	04APR1990	0.337	0.146	1.008	0.012	37.27	21.08	0.021316	0.000144
115	24JUL1990	0.437	0.159	1.022	0.002	38.50	22.06	0.025281	0.000004
116	12JUN1990	0.385	0.159	0.958	0.014	.	.	0.025281	0.000196
117	09APR1990	0.362	0.172	0.960	0.009	38.16	23.05	0.029584	0.000081
118	29AUG1990	0.424	0.200	0.999	0.013	36.99	21.01	0.040000	0.000169

Table A1.2

LOW RANGE DUPLICATE DATA

	SAMPLE	MATRIX	DIFFERENCE	SQUARE
1	TB-FTMC	TB	0.144	0.020740
2	T007-0176	EF	0.091	0.008280
3	T007-0177	EF	0.002	0.000000
4	T008-0217	SW	0.195	0.038030
5	T008-0215	EF	0.045	0.002020
6	T009-0238	SW	0.123	0.015130
7	T009-0256	EF	0.083	0.006890
8	T010-0282	SW	0.069	0.004760
9	T010-0283	SW	0.010	0.000100
10	T010-0286	SW	0.330	0.108900
11	T010-0300	SW	0.001	0.000000
12	T010-0301	EF	0.210	0.044100
13	T010-0304	SW	0.182	0.033120
14	T010-0317	EF	0.098	0.009600
15	T010-0320	SW	0.122	0.014880
16	T010-0285	SW	0.073	0.005330
17	T010-0287	SW	0.011	0.000120
18	T011-0354	EF	0.169	0.028560
19	T011-0356	SW	0.442	0.195360
20	T011-0360	SW	0.020	0.000400
21	T012-0415	TW	0.060	0.003600
22	LB-SMP-MA	SL	0.246	0.060520
23	INT-LEA-1	EF	0.079	0.006240
24	T013-0462	SW	0.337	0.113570
25	T018-0574	SW	0.041	0.001680
26	T021-0617	SW	0.043	0.001850
27	T022-0675	TW	0.028	0.000780
28	T025-0849	TW	0.007	0.000050
29	T030-0993	SW	0.163	0.026570
30	T030-1001	SW	0.289	0.083520
31	T033-1086	SW	0.163	0.026570
32	T033-1099	SW	0.143	0.020450
33	T034-1142	SW	0.495	0.245020
34	T034-1144	SW	0.001	0.000000
35	T034-1143	SW	0.302	0.091200
36	T034-1159	SW	0.069	0.004760
37	T034-1129	SW	0.039	0.001520
38	T037-1186	SW	0.117	0.013690
39	T037-1223	TW	0.378	0.142880
40		SW	0.001	0.000000
41	T042-1301	SW	0.967	0.935090
42		SW	0.001	0.000000
43	T044-1384	SW	0.240	0.057600
44	T044-1386	SW	0.826	0.682280
45	T045-1439	SW	0.232	0.053820
46	T047-1469	TW	0.366	0.133960
47	T047-1498	TW	0.156	0.024340
48	T049-1600	SW	0.110	0.012100
49	T049-1632	TW	0.336	0.112900
50	QC_SMP-00	TW	0.132	0.017420
51	T102-0073	TW	0.407	0.165650
52	T104-0089	SW	0.078	0.006080
53	T105-0092	SW	0.472	0.222780
54	T106-0120	SW	0.183	0.033490
55	T107-0136	SW	0.048	0.002300
56	T107-0162	SW	0.766	0.586760
57	T108-0255	SW	0.090	0.008100
58	T108-0259	SW	0.916	0.839060
59	T108-0262	SW	0.391	0.152880
60	T109-0339	SW	0.614	0.377000
61	T111-0428	SW	0.084	0.007060
62	T111-0426	SW	0.356	0.126740
63	T111-0561	SW	0.164	0.026900
64	T112-0574	SW	0.559	0.312480
65	T110-0418	SW	0.364	0.132500
66	T113-0626	SW	0.251	0.063000
67	T116-0713	SW	0.121	0.014640
68	T113-0626	SW	0.051	0.002600

Table A1.3

MID RANGE DUPLICATE DATA

	SAMPLE	MATRIX	DIFFERENCE	SQUARE
1	T007-0106	EF	0.153	0.023410
2	T007-0179	SW	0.001	0.000000
3	T008-0194	SW	0.001	0.000000
4	T009-0253	SW	0.607	0.368450
5	T010-0302	SW	0.425	0.180620
6	INT-LEACH	LE	0.268	0.071820
7	T013-0451	SW	0.553	0.305810
8	T017-0557	TW	0.105	0.011020
9	T019-0579	EF	0.105	0.011020
10	T021-0647	TW	1.861	3.463320
11	T022-0684	EF	1.130	1.276900
12	T023-0730	EF	0.300	0.090000
13	T023-0733	EF	0.163	0.026570
14	T023-0736	EF	0.105	0.011020
15	T028-0928	EF	0.025	0.000630
16	T028-0929	EF	0.605	0.366020
17	T033-1083	TW	0.393	0.154450
18	T034-1133	EF	0.979	0.958440
19	T034-1145	SW	0.212	0.044940
20	T049-1603	TW	0.363	0.131770
21	T049-1601	TW	0.112	0.012540
22	T102-0006	SW	0.443	0.196250
23	T102-0014	SW	0.615	0.378220
24	T102-0016	SW	0.120	0.014400
25	T107-0138	SW	0.518	0.268320
26	T107-0199	SW	0.172	0.029580
27	T107-0203	SW	0.205	0.042020
28	T108-0263	SW	0.074	0.005480
29	T108-0282	SW	0.053	0.002810
30	T110-0390	SW	0.234	0.054760
31	T111-0385	EF	0.085	0.007230
32	T112-0611	SW	0.484	0.234260
33	T112-0613	SW	0.472	0.222780

Table A1.4

2-Chlorobenzoic Acid Recovery

OBS	SAMPLE	MATRIX	RESULT	RECOVERY
1	T007-0174	SW	0.010	98.0
2	T007-0179	SW	0.090	100.4
3	T008-0195	SW	0.080	94.8
4	T008-0194	SW	0.070	94.1
5	T008-0216	SW	0.040	96.0
6	T009-0238	SW	0.000	94.9
7	T010-0282	SW	0.000	93.4
8	T010-0286	SW	0.040	98.6
9	T010-0300	SW	0.030	98.8
10	T010-0304	SW	0.410	98.7
11	T010-0320	SW	0.260	97.0
12	T010-0302	SW	0.355	100.9
13	T011-0330	SW	0.002	96.5
14	T011-0353	SW	0.006	102.4
15	T011-0355	SW	0.022	98.6
16	T011-0360	SW	0.019	103.9
17	T012-0402	SW	0.020	100.3
18	T013-0428	SW	0.013	98.1
19	T013-0462	SW	0.013	94.1
20	T013-0464	SW	0.030	100.9
21	T025-0828	SW	0.013	97.8
22	TO25-0850	SW	0.006	95.9
23	T029-0982	SW	0.087	100.2
24	T030-0993	SW	0.001	100.8
25	T030-1001	SW	0.018	96.2
26	T033-1086	SW	0.012	100.7
27	T033-1099	SW	0.002	99.8
28	T034-1142	SW	0.030	98.4
29	T034-1144	SW	0.027	88.1
30	T034-1132	SW	-0.003	102.6
31	T034-1143	SW	0.027	94.6
32	T034-1145	SW	0.053	88.6
33	T034-1159	SW	0.014	99.0
34	T034-1129	SW	0.001	90.6
35	MDL-DUP 2	SW	0.026	116.3
36	T037-1185	SW	0.012	97.5
37	T037-1186	SW	0.012	95.8
38	T037-1184	SW	0.008	92.9
39	T041-1287	SW	0.042	96.8
40	T042-1301	SW	0.006	91.9
41	T042-1334	SW	0.010	99.3
42	T044-1384	SW	0.012	105.5
43	T044-1386	SW	0.000	102.1
44	T045-1439	SW	0.014	100.3
45	T049-1600	SW	0.035	91.6
46	T102-0006	SW	0.305	94.8
47	T102-0010	SW	0.004	94.4
48	T102-0014	SW	0.059	95.4
49	T102-0016	SW	0.069	92.9
50	T104-0089	SW	0.044	97.4
51	T105-0092	SW	0.013	98.1
52	T106-0120	SW	0.001	94.8
53	T107-0136	SW	-0.003	102.7
54	T107-0162	SW	0.003	102.0
55	T107-0187	SW	0.150	108.7
56	T107-0199	SW	0.077	101.7
57	T107-0203	SW	0.124	98.1
58	T108-0255	SW	0.009	98.1
59	T108-0259	SW	0.006	105.7
60	T108-0262	SW	0.007	98.9
61	T108-0263	SW	0.239	98.6
62	T108-0282	SW	0.092	99.5
63	T109-0308	SW	0.001	99.8
64	T109-0339	SW	0.006	103.3
65	T110-0390	SW	0.074	102.3
66	T111-0428	SW	0.050	98.5
67	T111-0426	SW	0.036	104.7
68	T111-0561	SW	0.021	101.7
69	T112-0574	SW	0.045	95.9
70	T112-0588	SW	0.042	98.1
71	T110-0418	SW	0.375	101.9
72	T112-0611	SW	0.145	97.3
73	T112-0613	SW	0.658	94.7
74	T113-0626	SW	0.053	101.5
75	T112-0629	SW	0.015	98.5
76	T116-0713	SW	-0.001	102.6
77	T112-0613	SW	0.578	98.8
78	T113-0626	SW	0.045	96.0
79	T118-0792	SW	0.478	100.8
80	T118-0796	SW	0.191	104.8

Appendix 2

SAS Source Code for the Statistical Analysis of Quality Control Data

```
GOPTIONS DEV=HP7475A GSFNAME=OUT GSFMODE=REPLACE
COLORS=(BLACK BLACK BLACK BLACK BLACK BLACK BLACK BLACK);

**********  CALIBRATION FACTOR  **********;

FILENAME OUT 'CIJ0101.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS  NORMAL;
                VAR CAL_FAC ;
                LABLE CAL_FAC ='Calibration Factor';
                HISTOGRAM
                     /   NOLEGEND
                         NORMAL
                         MIDPOINTS=0.90 TO 1.10 BY 0.010 ;
RUN;

***********  CALIBRATION FACTOR VARIANCE  ***********;

FILENAME OUT 'CIJ0102.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS   NORMAL ;
                VAR CF_VAR ;
                LABLE  CF_VAR  =  'Calibration  Factor  Measurement
Variance';
                HISTOGRAM
                   /    NOLEGEND
                        GAMMA( ALPHA=0.5)
                        MIDPOINTS = 0.0 TO 0.0015 BY 0.0001;
RUN;

***********  METHOD BLANK  **********;

FILENAME OUT 'CIJ0104.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS   NORMAL ;
                WHERE BLANK < 0.8;
                VAR BLANK       ;
                LABEL BLANK = 'Blank (ug)';
                HISTOGRAM
                     / NORMAL
                       LOGNORMAL
                       GAMMA
                       MIDPOINTS = 0 TO 1.0 BY .05 ;
RUN;

**********  BLANK VARIANCE  **********;

FILENAME OUT 'CIJ0105.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS   NORMAL ;
                VAR BK_VAR       ;
                LABEL BK_VAR = 'Blank Variance' ;
                HISTOGRAM
                     /  NOLEGEND
                        GAMMA( ALPHA=1);
RUN;
```

```
**********  LOW RANGE DUPLICATES  **********;

FILENAME OUT 'CIJ0107.HPG';
PROC CAPABILITY DATA = I.DUPDATA   GRAPHICS;
                WHERE SQUARE < 0.5;
                VAR SQUARE ;
                LABEL SQUARE = 'Duplicate Differences Squared' ;
                HISTOGRAM
                     /  NOLEGEND
                        GAMMA ( ALPHA=0.5 )
                        MIDPOINTS= 0.025 TO 0.525 BY 0.05 ;
RUN;

**********  MID RANGE DUPLICATES  **********;

FILENAME OUT 'CIJ0006.HPG';
PROC CAPABILITY DATA = I.DUPMID  GRAPHICS;
                WHERE SQUARE < 0.9;
                VAR SQUARE ;
                LABEL SQUARE = 'Duplicate Differences Squared' ;
                HISTOGRAM
                     /   NOLEGEND
                         GAMMA  (ALPHA=0.5)
                         MIDPOINTS= 0.0 TO 1.0 BY 0.05;
RUN;

**********  2-CHLOROBENZOIC ACID RECOVERY  **********;

FILENAME OUT 'CIJ0108.HPG';
PROC CAPABILITY DATA = I.RECVDATA   GRAPHICS   NORMAL ;
                WHERE RECOVERY > 90 AND RECOVERY < 110;
                VAR RECOVERY       ;
                LABEL RECOVERY = 'Percent Recovery';
                HISTOGRAM
                     /   NOLEGEND
                         NORMAL
                         MIDPOINTS= 90 TO 110 BY 1;
RUN;

**********     QUALITY   CONTROL   STANDADARDS   VRS   CALIBRATION
**********;

DATA TWO;
     SET I.NEWDATA;
     WHERE DATE > '01JAN91'D;
RUN;

FILENAME OUT 'CIJ0109.HPG';
PROC GPLOT DATA=TWO;
          PLOT CAL_FAC * QCAPLUS;
RUN;

FILENAME OUT 'CIJ0110.HPG';
PROC GPLOT DATA=TWO;
          PLOT CAL_FAC * QCAMINUS;
RUN;
```

```
PROC CORR DATA=TWO PEARSON ;
          VAR CAL_FAC QCAPLUS QCAMINUS;
RUN;

**********  CORRELATION OF VARIATION AND MEASURMENT **********;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR CAL_FAC CF_VAR;
RUN;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR BLANK BK_VAR;
RUN;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR CAL_FAC CF_VAR;
RUN;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR BLANK BK_VAR;
RUN;

PROC CAPABILITY DATA=TWO NORMAL GRAPHICS ;
                VAR QCAPLUS;
                HISTOGRAM /NORMAL ;
RUN;

PROC CAPABILITY DATA=TWO NORMAL GRAPHICS ;
                VAR QCAMINUS;
                HISTOGRAM /NORMAL ;
RUN;

PROC RANK  DATA=I.NEWDATA OUT=RANKDATA ;
           VAR CAL_FAC  CF_VAR  BLANK  BK_VAR;
           RANKS CF_RANK CFV_RANK BK_RANK BKV_RANK;
RUN;

FILENAME OUT 'CIJ0103.HPG';
PROC GPLOT DATA=RANKDATA;
           LABEL CFV_RANK = 'Rank of Calibration Factor Variance'
                  CF_RANK = 'Rank of Calibration Factor';
           PLOT CFV_RANK * CF_RANK;
RUN;

FILENAME OUT 'CIJ0106.HPG';
PROC GPLOT DATA=RANKDATA;
           LABEL BKV_RANK = 'Rank of Blank Variance'
                  BK_RANK = 'Rank of Blank';
           PLOT BKV_RANK * BK_RANK;
RUN;
```

Appendix 3

SAS® Reports

```
                                  CAPABILITY

Variable=CAL_FAC       Calibration Factor

                                   Moments

                   N                118  Sum Wgts         118
                   Mean        0.992856  Sum          117.157
                   Std Dev     0.025157  Variance    0.000633
                   Skewness    0.262153  Kurtosis    -0.30599
                   USS         116.3941  CSS         0.074049
                   CV           2.53384  Std Mean    0.002316
                   T:Mean=0    428.7083  Prob>|T|      0.0000
                   Sgn Rank      3510.5  Prob>|S|      0.0000
                   Num ^= 0         118
                   W:Normal    0.974054  Prob<W         0.205

                               Quantiles(Def=5)

                   100% Max       1.061     99%         1.06
                    75% Q3        1.012     95%        1.032
                    50% Med       0.991     90%        1.024
                    25% Q1        0.975     10%         0.96
                     0% Min       0.943      5%        0.952
                                             1%        0.946
                   Range          0.118
                   Q3-Q1          0.037
                   Mode           0.975


                                   Extremes

                      Lowest    Obs     Highest    Obs
                       0.943(       7)    1.037(      60)
                       0.946(      82)    1.039(      20)
                       0.946(      41)    1.046(     102)
                       0.946(      10)     1.06(      54)
                       0.951(     108)    1.061(      28)


                         Fitted Distribution: Normal

                Parameters                    Goodness-of-Fit

       Mean (Mu)          0.99285593   Chi-Square         9.59857846
       Std Dev (Sigma)    0.02515738   Df                         10
                                       Pr > Chi-Square    0.47638814

                                  Quantiles

                  Percent    Obs Quantile    Est Quantile

                     1.0        0.94600         0.93433
                     5.0        0.95200         0.95148
                    10.0        0.96000         0.96062
                    25.0        0.97500         0.97589
                    50.0        0.99100         0.99286
                    75.0        1.01200         1.00982
                    90.0        1.02400         1.02510
                    95.0        1.03200         1.03424
                    99.0        1.06000         1.05138
```

```
                                  CAPABILITY

Variable=CF_VAR        Calibration Factor Measurement Variance

                                   Moments

                   N                 118  Sum Wgts         118
                   Mean         0.000173  Sum         0.020471
                   Std Dev      0.000253  Variance    6.422E-8
                   Skewness     2.413302  Kurtosis    6.883897
                   USS          0.000011  CSS         7.514E-6
                   CV           146.0803  Std Mean    0.000023
                   T:Mean=0     7.436172  Prob>|T|      0.0000
                   Sgn Rank       3510.5  Prob>|S|      0.0000
                   Num ^= 0          118
                   W:Normal     0.701532  Prob<W         0.000


                               Quantiles(Def=5)

                   100% Max   0.001444      99%    0.001089
                    75% Q3    0.000225      95%    0.000729
                    50% Med   0.000081      90%    0.000529
                    25% Q1     0.00001      10%        4E-6
                     0% Min       1E-6       5%        1E-6
                                             1%        1E-6
                   Range      0.001443
                   Q3-Q1      0.000215
                   Mode           1E-6

                                   Extremes

                      Lowest    Obs     Highest    Obs
                        1E-6(      96) 0.000729(     103)
                        1E-6(      85)   0.0009(      47)
                        1E-6(      81) 0.001024(      33)
                        1E-6(      61) 0.001089(      93)
                        1E-6(      39) 0.001444(      95)


                          Fitted Distribution: Gamma


                Parameters                    Goodness-of-Fit

       Threshold (Theta)            0   Chi-Square           15.0376603
       Scale (Sigma)       0.00034697   Df                           13
       Shape (Alpha)              0.5   Pr > Chi-Square      0.30500763
       Est Mean            0.00017348
       Est Std Dev         0.00024534

                                  Quantiles

                  Percent     Obs Quantile     Est Quantile

                     1.0        0.000001        0.00000003
                     5.0        0.000001        0.00000068
                    10.0        0.000004        0.00000274
                    25.0        0.000010        0.00001761
                    50.0        0.000081        0.00007892
                    75.0        0.000225        0.00022957
                    90.0        0.000529        0.00046937
                    95.0        0.000729        0.00066643
                    99.0        0.001089        0.00115104
```

```
                                  CAPABILITY

Variable=BLANK         Blank (ug)

                                   Moments

                   N                116  Sum Wgts         116
                   Mean        0.428759  Sum           49.736
                   Std Dev     0.110549  Variance    0.012221
                   Skewness    0.466144  Kurtosis    0.404717
                   USS         22.73016  CSS         1.405425
                   CV          25.78351  Std Mean    0.010264
                   T:Mean=0    41.77216  Prob>|T|      0.0000
                   Sgn Rank        3393  Prob>|S|      0.0000
                   Num ^= 0         116
                   W:Normal    0.965653  Prob<W         0.043

                               Quantiles(Def=5)

                   100% Max      0.755     99%        0.737
                    75% Q3       0.486     95%        0.644
                    50% Med      0.414     90%        0.587
                    25% Q1      0.3645     10%        0.296
                     0% Min      0.191      5%        0.242
                                            1%         0.21

                   Range         0.564
                   Q3-Q1        0.1215
                   Mode          0.402

                                   Extremes

                      Lowest    Obs     Highest    Obs
                       0.191(      77)    0.647(      79)
                        0.21(      37)    0.649(      93)
                        0.22(      24)    0.658(      78)
                       0.235(      53)    0.737(      97)
                       0.241(      10)    0.755(      60)

                         Fitted Distribution: Normal


                Parameters                    Goodness-of-Fit

       Mean (Mu)          0.42875862   Chi-Square         26.1244077
       Std Dev (Sigma)    0.11054903   Df                          9
                                       Pr > Chi-Square    0.00194938

                                  Quantiles

                  Percent    Obs Quantile    Est Quantile

                     1.0        0.21000         0.17158
                     5.0        0.24200         0.24692
                    10.0        0.29600         0.28708
                    25.0        0.36450         0.35419
                    50.0        0.41400         0.42876
                    75.0        0.48600         0.50332
                    90.0        0.58700         0.57043
                    95.0        0.64400         0.61060
                    99.0        0.73700         0.68593
                  Fitted Distribution: Lognormal

           Parameters                      Goodness-of-Fit

Threshold (Theta)            0   Chi-Square          22.1881827
Scale (Zeta)        -0.8806807   Df                           9
Shape (Sigma)       0.26432587   Pr > Chi-Square     0.00830133
Est Mean            0.42923678
Est Std Dev         0.11546932

                            Quantiles

             Percent    Obs Quantile    Est Quantile

               1.0         0.21000         0.22412
               5.0         0.24200         0.26835
              10.0         0.29600         0.29540
              25.0         0.36450         0.34681
              50.0         0.41400         0.41450
              75.0         0.48600         0.49540
              90.0         0.58700         0.58162
              95.0         0.64400         0.64025
              99.0         0.73700         0.76662

                    Fitted Distribution: Gamma

           Parameters                      Goodness-of-Fit

Threshold (Theta)            0   Chi-Square          20.4930817
Scale (Sigma)       0.02868257   Df                           9
Shape (Alpha)       14.9484022   Pr > Chi-Square     0.01510167
Est Mean            0.42875862
Est Std Dev          0.1108959

                            Quantiles

             Percent    Obs Quantile    Est Quantile

               1.0         0.21000         0.21342
               5.0         0.24200         0.26405
              10.0         0.29600         0.29419
              25.0         0.36450         0.34969
              50.0         0.41400         0.41924
              75.0         0.48600         0.49746
              90.0         0.58700         0.57560
              95.0         0.64400         0.62596
              99.0         0.73700         0.72793
```

```
                                  CAPABILITY

Variable=BK_VAR        Blank Variance

                                   Moments

                   N                118  Sum Wgts         118
                   Mean        0.006574  Sum         0.775781
                   Std Dev     0.007184  Variance    0.000052
                   Skewness    1.760734  Kurtosis    4.000298
                   USS         0.011139  CSS         0.006039
                   CV           109.276  Std Mean    0.000661
                   T:Mean=0    9.940685  Prob>|T|      0.0000
                   Sgn Rank      3510.5  Prob>|S|      0.0000
                   Num ^= 0         118
                   W:Normal    0.820725  Prob<W         0.000

                               Quantiles(Def=5)

                   100% Max       0.04     99%     0.029584
                    75% Q3    0.009801     95%     0.021025
                    50% Med   0.004831     90%     0.015876
                    25% Q1    0.001089     10%     0.000225
                     0% Min       9E-6      5%     0.000081
                                            1%         9E-6

                   Range      0.039991
                   Q3-Q1      0.008712
                   Mode       0.000081


                                   Extremes

                      Lowest    Obs     Highest    Obs
                        9E-6(       2) 0.021316(     114)
                        9E-6(       1) 0.025281(     115)
                    0.000016(       3) 0.025281(     116)
                    0.000081(       6) 0.029584(     117)
                    0.000081(       5)     0.04(     118)

                          Fitted Distribution: Gamma


                Parameters                    Goodness-of-Fit

       Threshold (Theta)           0   Chi-Square         8.52059788
       Scale (Sigma)      0.00657442   Df                          7
       Shape (Alpha)               1   Pr > Chi-Square     0.2889302
       Est Mean           0.00657442
       Est Std Dev        0.00657442

                                  Quantiles

                  Percent    Obs Quantile    Est Quantile

                      1.0       0.000009         0.00007
                      5.0       0.000081         0.00034
                     10.0       0.000225         0.00069
                     25.0       0.001089         0.00189
                     50.0       0.004831         0.00456
                     75.0       0.009801         0.00911
                     90.0       0.015876         0.01514
                     95.0       0.021025         0.01970
                     99.0       0.029584         0.03028
```

```
                                CAPABILITY

                 Low Range Duplicate Differences Squared

                                 Moments

            N                64  Sum Wgts          64
            Mean       0.053862  Sum         3.447153
            Std Dev    0.079998  Variance      0.0064
            Skewness   2.133838  Kurtosis    4.775936
            USS        0.588854  CSS         0.403185
            CV         148.5255  Std Mean        0.01
            T:Mean=0    5.38628  Prob>|T|      0.0000
            Sgn Rank       1040  Prob>|S|      0.0000
            Num ^= 0         64


                             Quantiles(Def=5)

            100% Max   0.376996       99%     0.376996
             75% Q3    0.073261       95%     0.222784
             50% Med   0.016276       90%     0.152881
             25% Q1    0.003101       10%       0.0001
              0% Min       1E-6        5%         1E-6
                                       1%         1E-6
            Range      0.376995
            Q3-Q1       0.07016
            Mode           1E-6


                                 Extremes

               Lowest    Obs     Highest    Obs
                 1E-6(      41) 0.195364(      19)
                 1E-6(      40) 0.222784(      51)
                 1E-6(      34) 0.245025(      33)
                 1E-6(      11) 0.312481(      60)
                 4E-6(       3) 0.376996(      56)

                      Fitted Distribution: Gamma

            Parameters                        Goodness-of-Fit

  Threshold (Theta)              0   Chi-Square          6.22198531
  Scale (Sigma)         0.10772353   Df                           6
  Shape (Alpha)                0.5   Pr > Chi-Square     0.39878831
  Est Mean              0.05386177
  Est Std Dev           0.07617204

                                Quantiles

           Percent    Obs Quantile    Est Quantile

               1.0      0.000001        0.000008
               5.0      0.000001        0.000212
              10.0      0.000100        0.000851
              25.0      0.003101        0.005469
              50.0      0.016276        0.024504
              75.0      0.073261        0.071275
              90.0      0.152881        0.145725
              95.0      0.222784        0.206908
              99.0      0.376996        0.357367
```

```
                              CAPABILITY

                  Mid Range Duplicate Differences Squared

                               Moments

                  N                  30  Sum Wgts          30
                  Mean         0.108874  Sum         3.266231
                  Std Dev      0.126293  Variance     0.01595
                  Skewness     1.029248  Kurtosis    -0.29855
                  USS          0.818157  CSS         0.462548
                  CV           115.9989  Std Mean    0.023058
                  T:Mean=0     4.721791  Prob>|T|      0.0001
                  Sgn Rank        232.5  Prob>|S|      0.0000
                  Num ^= 0           30


                            Quantiles(Def=5)

                  100% Max  0.378225        99%      0.378225
                   75% Q3   0.196249        95%      0.368449
                   50% Med  0.043484        90%      0.335917
                   25% Q1   0.011025        10%      0.001717
                    0% Min      1E-6         5%          1E-6
                                             1%          1E-6
                  Range     0.378224
                  Q3-Q1     0.185224
                  Mode      0.011025


                               Extremes

                     Lowest    Obs     Highest    Obs
                       1E-6(     3) 0.268324(     22)
                       1E-6(     2) 0.305809(      7)
                   0.000625(    13) 0.366025(     14)
                   0.002809(    26) 0.368449(      4)
                   0.005476(    25) 0.378225(     20)

                       Fitted Distribution: Gamma

            Parameters                       Goodness-of-Fit

    Threshold (Theta)              0  Chi-Square          7.71422645
    Scale (Sigma)         0.21774873  Df                           7
    Shape (Alpha)                0.5  Pr > Chi-Square     0.35846631
    Est Mean              0.10887437
    Est Std Dev           0.15397161

                              Quantiles

                 Percent     Obs Quantile    Est Quantile

                   1.0         0.000001        0.00002
                   5.0         0.000001        0.00043
                  10.0         0.001717        0.00172
                  25.0         0.011025        0.01105
                  50.0         0.043484        0.04953
                  75.0         0.196249        0.14407
                  90.0         0.335917        0.29456
                  95.0         0.368449        0.41824
                  99.0         0.378225        0.72237
```

```
                                  CAPABILITY

Variable=RECOVERY      Percent Recovery

                                   Moments

                   N                 77  Sum Wgts          77
                   Mean        98.61948  Sum           7593.7
                   Std Dev     3.574288  Variance    12.77554
                   Skewness    0.157161  Kurtosis    -0.02111
                   USS         749857.7  CSS         970.9408
                   CV          3.624323  Std Mean    0.407328
                   T:Mean=0    242.1132  Prob>|T|      0.0000
                   Sgn Rank      1501.5  Prob>|S|      0.0000
                   Num ^= 0          77
                   W:Normal    0.988085  Prob<W         0.925

                               Quantiles(Def=5)

                   100% Max      108.7     99%        108.7
                    75% Q3       100.9     95%        104.8
                    50% Med       98.6     90%        102.7
                    25% Q1          96     10%         94.1
                     0% Min       90.6      5%         92.9
                                            1%         90.6

                   Range          18.1
                   Q3-Q1           4.9
                   Mode           98.1


                                   Extremes

                      Lowest    Obs     Highest    Obs
                        90.6(      32)    104.7(      64)
                        91.6(      42)    104.8(      77)
                        91.9(      37)    105.5(      39)
                        92.9(      46)    105.7(      56)
                        92.9(      35)    108.7(      52)

                         Fitted Distribution: Normal


                Parameters                    Goodness-of-Fit

       Mean (Mu)          98.6194805   Chi-Square         13.3495811
       Std Dev (Sigma)    3.57428826   Df                         16
                                       Pr > Chi-Square     0.6470463

                                  Quantiles

                  Percent    Obs Quantile    Est Quantile

                     1.0        90.6000         90.3044
                     5.0        92.9000         92.7403
                    10.0        94.1000         94.0388
                    25.0        96.0000         96.2087
                    50.0        98.6000         98.6195
                    75.0       100.9000        101.0303
                    90.0       102.7000        103.2001
                    95.0       104.8000        104.4987
                    99.0       108.7000        106.9345
```

```
                         CORRELATION ANALYSIS

               3 'VAR' Variables:  CAL_FAC  QCAPLUS  QCAMINUS

                           Simple Statistics

Variable              N          Mean       Std Dev        Median

CAL_FAC              33       1.00258       0.02167       1.00200
QCAPLUS              33      39.17606       1.22829      39.37000
QCAMINUS             33      19.91212       1.00179      20.11000

          Simple Statistics

Variable        Minimum       Maximum

CAL_FAC         0.94600       1.03900
QCAPLUS        36.60000      41.74000
QCAMINUS       17.88000      21.29000

 Pearson Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 33

                        CAL_FAC          QCAPLUS         QCAMINUS

  CAL_FAC               1.00000         -0.48737         -0.18873
                         0.0             0.0040           0.2929

  QCAPLUS              -0.48737          1.00000          0.77891
                         0.0040          0.0              0.0001

  QCAMINUS             -0.18873          0.77891          1.00000
                         0.2929          0.0001           0.0

Spearman Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 33

                        CAL_FAC          QCAPLUS         QCAMINUS

  CAL_FAC               1.00000         -0.43770         -0.10331
                         0.0             0.0109           0.5672

  QCAPLUS              -0.43770          1.00000          0.74574
                         0.0109          0.0              0.0001

  QCAMINUS             -0.10331          0.74574          1.00000
                         0.5672          0.0001           0.0
                         CORRELATION ANALYSIS

               2 'VAR' Variables:  CAL_FAC   CF_VAR

                           Simple Statistics

Variable              N           Mean        Std Dev         Median

CAL_FAC             118        0.99286        0.02516        0.99100
CF_VAR              118      0.0001735      0.0002534      0.0000810

          Simple Statistics

Variable       Minimum        Maximum

CAL_FAC        0.94300        1.06100
CF_VAR            1E-6        0.00144

Spearman Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 118

                         CAL_FAC            CF_VAR

           CAL_FAC       1.00000          -0.03556
                          0.0               0.7023

           CF_VAR       -0.03556           1.00000
                          0.7023            0.0


                         CORRELATION ANALYSIS

               2 'VAR' Variables:  BLANK    BK_VAR

                           Simple Statistics

Variable              N           Mean        Std Dev         Median

BLANK               118        0.43717        0.12739        0.42400
BK_VAR              118        0.00657        0.00718        0.00483

          Simple Statistics

Variable       Minimum        Maximum

BLANK          0.19100        0.99300
BK_VAR            9E-6        0.04000

Spearman Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 118

                            BLANK            BK_VAR

            BLANK        1.00000          -0.12820
                          0.0               0.1665

            BK_VAR      -0.12820           1.00000
                          0.1665            0.0
```

```
                                 CAPABILITY

Variable=QCAPLUS

                                  Moments

                N                  33  Sum Wgts          33
                Mean         39.17606  Sum          1292.81
                Std Dev      1.228291  Variance      1.5087
                Skewness     -0.20089  Kurtosis    -0.38139
                USS          50695.48  CSS         48.27839
                CV           3.135311  Std Mean    0.213818
                T:Mean=0     183.2215  Prob>|T|      0.0000
                Sgn Rank        280.5  Prob>|S|      0.0000
                Num ^= 0           33
                W:Normal     0.981238  Prob<W         0.858

                              Quantiles(Def=5)

                100% Max        41.74       99%        41.74
                 75% Q3         40.06       95%        41.15
                 50% Med        39.37       90%        40.58
                 25% Q1         38.52       10%        37.56
                  0% Min         36.6        5%        36.87
                                             1%         36.6
                Range            5.14
                Q3-Q1            1.54
                Mode             36.6

                                  Extremes

                  Lowest     Obs      Highest     Obs
                   36.6(       9)      40.48(      10)
                  36.87(       8)      40.58(       3)
                  37.51(      31)      40.64(      19)
                  37.56(      29)      41.15(       1)
                  37.58(      27)      41.74(       4)


                       Fitted Distribution: Normal


             Parameters                    Goodness-of-Fit

       Mean (Mu)          39.1760606   Chi-Square             2.0733325
       Std Dev (Sigma)    1.22829134   Df                             3
                                       Pr > Chi-Square       0.55732659

                                 Quantiles

               Percent     Obs Quantile     Est Quantile

                   1.0          36.6000          36.3186
                   5.0          36.8700          37.1557
                  10.0          37.5600          37.6019
                  25.0          38.5200          38.3476
                  50.0          39.3700          39.1761
                  75.0          40.0600          40.0045
                  90.0          40.5800          40.7502
                  95.0          41.1500          41.1964
                  99.0          41.7400          42.0335
```

```
                                  CAPABILITY

Variable=QCAMINUS
                                   Moments

                   N                   33  Sum Wgts            33
                   Mean          19.91212  Sum              657.1
                   Std Dev       1.001795  Variance      1.003592
                   Skewness      -0.44935  Kurtosis      -0.94757
                   USS           13116.37  CSS           32.11495
                   CV            5.031079  Std Mean       0.17439
                   T:Mean=0      114.1815  Prob>|T|        0.0000
                   Sgn Rank         280.5  Prob>|S|        0.0000
                   Num ^= 0            33
                   W:Normal      0.923324  Prob<W           0.027

                               Quantiles(Def=5)

                   100% Max       21.29     99%        21.29
                    75% Q3        20.51     95%        21.24
                    50% Med       20.11     90%         21.2
                    25% Q1        19.02     10%        18.64
                     0% Min       17.88      5%        18.11
                                             1%        17.88
                   Range           3.41
                   Q3-Q1           1.49
                   Mode           19.83

                                   Extremes

                      Lowest    Obs     Highest    Obs
                       17.88(      30)    21.11(        4)
                       18.11(      29)     21.2(        7)
                       18.35(      22)    21.22(       24)
                       18.64(       9)    21.24(       19)
                       18.65(      15)    21.29(        1)


                         Fitted Distribution: Normal


                Parameters                    Goodness-of-Fit

       Mean (Mu)          19.9121212   Chi-Square          7.97620782
       Std Dev (Sigma)    1.00179451   Df                           3
                                       Pr > Chi-Square     0.04650599

                                  Quantiles

                  Percent    Obs Quantile    Est Quantile

                     1.0        17.8800         17.5816
                     5.0        18.1100         18.2643
                    10.0        18.6400         18.6283
                    25.0        19.0200         19.2364
                    50.0        20.1100         19.9121
                    75.0        20.5100         20.5878
                    90.0        21.2000         21.1960
                    95.0        21.2400         21.5599
                    99.0        21.2900         22.2426
```

Appendix 4

Method E128.0 for Adsorbable Organic Halide

ADSORBABLE ORGANIC HALIDES IN PULP MILL EFFLUENT

1. Scope and Application

1.1 This method describes the procedure for measuring adsorbable organic halide (AOX) in bleached kraft mill effluent. In these effluents, the AOX present is almost exclusively organically bound chlorine even though the method is sensitive to organic bromine and iodine as well.

1.2 The term organic chlorine is used throughout this method, and includes all organically bound halogens.

1.3 This method is designed to give results consistent with the Scandinavian Pulp, Paper and Board Testing Method SCAN 9:89. This method determines organic chlorine in both dissolved and suspended material.

1.4 This method is applicable to samples with an AOX concentration range of 25 to 400 μg/L of effluent as submitted, measured as chloride. Samples with higher AOX concentrations must be diluted prior to analysis.

2. Summary of Method

2.1 This method consists of three steps.

2.1.1 The adsorption of organic compounds in a 100 mL sample onto granular activated carbon (GAC) and the displacement of adsorbed inorganic chloride with nitrate ions.

2.1.2 The combustion of the GAC and suspended material to convert all the organic chlorine to hydrogen chloride.

2.1.3 A titration of resulting chloride with microcoulometrically generated silver ion.

3. Interferences

3.1 Organically bound chlorine contamination of sample, reagent water, and GAC will cause elevated background, and greater variation of the background. Some sources of organically bound chlorine are volatile chlorinated laboratory solvents, and halogenated compounds present in improperly prepared reagent waters.

3.2 Bound chlorine present in membrane filters can cause an increase in the magnitude and variation of the background.

3.3 To avoid contamination, all analyses should be performed in an environment where chlorinated solvents can be excluded. All material used in the analysis should be stored in a desiccator over activated carbon.

3.4 Inorganic chloride can be detected when present in the diluted sample in concentrations greater than 1.0 mMole (5.8 mg/100mL as sodium chloride; 3.5 mg/100 mL chloride).

3.5 When the sample has a high concentration of dissolved organic carbon, the GAC can become saturated before adsorbing all the organic halide present, leading to low recoveries.

4. Sample Collection, Preservation, and Handling

4.1 Samples must be collected in 500 mL polyethylene bottles and filled with no head space. Samples must be acidified with nitric acid to a pH less than 2.1 and greater than 1.5.

4.2 If the sample contains active chlorine[1], add one crystal of sodium sulphite to neutralize the chlorine. It is important that the sample be acidified prior to the addition of sodium sulphite, and that the addition is recorded.

4.3 A trip blank of ASTM Type II reagent water or better, acidified to pH 1.5 to 2.1 with nitric acid, must be prepared.

4.4 Samples must be iced or refrigerated at 4°C upon collection and maintained at 4°C until analysis.

4.5 Samples must be analyzed within 14 days of sampling.

5. Safety

5.1 The laboratory maintains material safety data sheets (MSDS) for all chemicals involved in this method. This material is readily available to all personnel involved in the chemical analysis.

5.2 Additional references to laboratory safety have been identified for the information of the analysts.

6. Apparatus and Materials

6.1 Sampling Equipment.

6.1.1 Sampling bottle - 500 mL polyethylene bottle with screw cap.

---

[1] Most effluents will contain no active chlorine. To determine if any is present, add one crystal of potassium iodide, then two drops of a 1% starch solution to 10 mL of the effluent. An immediate change in colour to blue, upon addition of the starch solution, indicates that active chlorine is present.

6.1.2 Nitric acid - 50% nitric acid to acidify the sample. One 5 mL ampoule provided by the laboratory added to the 500 mL sample usually achieves the desired pH.

6.1.3 pH Meter - pH meter accurate to ± 0.1 pH units.

6.1.4 Starch solution - 1% starch solution in reagent water.

6.1.5 Sodium sulphite - ACS reagent grade (crystal).

6.1.6 Potassium iodide - ACS reagent grade (granular).

6.1.7 Reagent water - ASTM Type II or better for trip blank.

6.1.8 Cooler and ice.

6.1.9 Glass vial or test tube.

6.2 Glassware.

6.2.1 Transfer pipettes, 5.00 mL, 10.00 mL, and 20.00 mL.

6.2.2 Syringes, 10.0 µL, 25µL and 50 µL gas tight.

6.2.3 Volumetric flasks, 50.00 mL and 100.00 mL.

6.2.4 Filtering apparatus, sintered glass filter supports for 25 mm membrane filters, vacuum manifold.

6.2.5 Conical flasks, 250 mL with ground glass stopper.

6.3 Equipment.

6.3.1 Orbital Stirrer, adjustable to > 120 cycles per second.

6.3.2 Vacuum source, suitable for vacuum filtration.

6.3.3 pH Meter, accurate to ± 0.01 pH units, and associated calibration buffers.

6.3.4 Polycarbonate membrane filters, 0.40 µm pore size, 25 mm diameter.

6.3.5 Measuring scoop, designed to deliver 40 mg of GAC.

6.3.6 Analytical balance, capable of weighing ± 0.0001 g.

6.3.7 AOX Microcoulometric System, capable of determining 0.1 to 50 µg Cl. This includes any additional apparatus and chemicals specified by the manufacturer (i.e. electrode and electrolytes).

6.4 Chemicals.

6.4.1 Sodium chloride - ACS reagent grade.

6.4.2 Sodium nitrate - ACS reagent grade.

6.4.3 Sodium bicarbonate - ACS reagent grade.
6.4.4 Silver nitrate - ACS reagent grade.
6.4.5 2,4,6-Trichlorophenol - >98% purity.
6.4.6 2-Chlorobenzoic acid - >98% purity.
6.4.7 Nitric acid - 1.40 g/mL.
6.4.8 Methanol - distilled in glass, chlorine free.
6.4.9 Reagent water - ASTM Type II (or better) reagent water.
6.4.10 Granular activated carbon, zero chlorine.

7. Reagents

7.1 All aqueous reagent solutions are prepared using ASTM Type II (or better) reagent water. Solutions in methanol are prepared using distilled in glass, chlorine free methanol.

7.2 Dilute nitric acid - 1.4 mL of nitric acid diluted to 1000 mL with reagent water.

7.3 Nitrate solution - dissolve 17 g of sodium nitrate in 1000 mL of dilute nitric acid.

7.4 Washing solution - dilute 100 mL of nitrate solution to 1000 mL with reagent water.

7.5 Sodium chloride solution - dissolve 0.1200 g sodium chloride in 200.0 mL reagent water.

7.6 Silver nitrate solution - dissolve 0.1700 g silver nitrate in 100.0 mL reagent water.

7.7 2,4,6-Trichlorophenol solution - dissolve 0.1857 g 2,4,6-trichlorophenol in 100.0 mL methanol (1.000 µg Cl/µL).

7.8 2-Chlorobenzoic acid - dissolve 0.1102 g of 2-chlorobenzoic acid in 50.0 mL methanol (0.500 µg Cl/µL).

7.9 2,4,6-Trichlorophenol quality control A (QCA) solution - dissolve 0.5520 g of 2,4,6-trichlorophenol in 100.0 mL methanol.

7.10 2,4,6-Trichlorophenol quality control B (QCB) solution - dissolve 0.1380 g of 2,4,6-trichlorophenol in 100.0 mL of methanol.

8. Sample Adsorption[1]

8.1 All samples are analyzed at least twice. The dilution used for one determination is double that of the other.

8.2 This method provides for the analysis of the organically bound chlorine in suspended material. Samples must be shaken vigorously to suspend the particulate material prior to aliquots being taken.

8.3 Dilute the sample to the working range 25-400 µg/L of the instrument (25-400 µg/L AOX), using dilute nitric acid.[2] All dilutions are performed using aliquots of not less than 5 mL into dilute nitric acid. When dilutions of greater than 1 to 10 are required, the dilution must be done in multiple stages, each no more than 1 to 10. All but the final dilutions, are performed in volumetric flasks. Final dilutions are performed in 250 mL conical flasks. Typical bleached kraft mill effluents require a dilution of either 10 mL or 20 mL to 100 mL followed by dilutions of 5 mL and 10 mL[2] to 100 mL.

---

[1] Requirements for an organic chlorine free laboratory environment, specified in Sections 3.1 and 3.3 must be strictly adhered to.

[2] This method requires analysis at two dilutions, one double the other.

8.4 All dilutions are recorded and the final effective volume of the sample is calculated as:

effective volume = dilution 1 x dilution 2...x100 mL.

8.5 Five mL of nitrate solution and 40 mg of GAC (using scoop specified in Section 6.3) are added to diluted sample in the 250 mL conical flasks. Flasks are then capped and agitated by orbital shaker for not less than 1 hour, at a rate greater than 120 cycles per second.

8.6 The contents of the 250 mL flask are filtered, collecting the GAC and insoluble material on a 0.40 µm polycarbonate filter (25 mm diameter). The flask is rinsed with small aliquots of wash solution (the combined aliquots totalling 25 mL). The interior wall of the filter unit is rinsed so that all the particulate material is collected on the membrane filter. Great care must be taken not to draw large volumes of air over the filter bed.

8.7 A minimum of two method blanks (dilute nitric acid) must be analyzed per day. The method blank is prepared using only dilute nitric and nitrate solution, with the GAC, in the adsorption step. The GAC is collected by filtration using the same method and techniques as the samples.

8.8 One sample fortified with 2-chlorobenzoic acid (standard addition) must be analyzed per day (see Section 13.4). The fortified sample is prepared by adding 20 µL of 2-chlorobenzoic acid solution to the final dilution of the sample to the 250 mL conical flask, prior to the addition of GAC.

9. Cleanup

Not applicable for this method.

10. Sample Combustion and Chloride Determination by Microcoulometry.

10.1 Twenty µL of the test titrations of sodium chloride solution (see Section 7.5) injected directly into the microcoulometric cell are performed to determine the coulometer operating parameters.

10.2 At daily startup and after routine cell maintenance (changing electrolyte and polishing working electrode), 10 µL of 2,4,6-trichlorophenol solution, injected directly into the sample boat must be analyzed (two analysis after daily startup). Recovery of AOX (as chloride) must all be within the range of 95 to 105%, with a standard deviation no greater than 3%.

10.3 The filter membrane, containing the GAC and filtered material, is transferred quantitatively to the sample boat, and is combusted at 950°C under an atmosphere of oxygen, in the pyrolysis oven. The microcoulometer and cell are operated in accordance with the manufacturer specifications. Any exceptions must be noted. Results are recorded as µg chloride detected. This is the instrument AOX.

11. Calibration

11.1 A calibration curve over the full operating range of the method (2.5 to 40 µg AOX as chloride) must be developed. Aliquots of 2,4,6-trichlorophenol solution of 5, 10, 15, 25, and 40 µL are directly injected into the sample boat and analyzed. Calibration curves must be run after any instrument reconfiguration and after major maintenance (i.e. pyrolysis tube and/or packing replacement, electrode replacement)[1].

---

[1] After cell maintenance such as electrode replacement, the analyst may wish to verify cell and microcoulometer operation with direct injection of sodium chloride solution into the cell. These analyses do not constitute calibration.

11.2 Daily calibration injections of 10 µL 2,4,6-trichlorophenol solution (discussed in 10.2) are used for routine calibration. The calibration factor is the mean of all results divided by the amount determined (approximately 10 µg AOX as chloride).

12. Calculation

12.1 The daily calibration factor[1] is calculated as the mean of the calibration determinations (Section 11.2).

12.2 The blank[2] AOX is calculated as the mean of the blank determinations (Section 8.7).

12.3 Calibrated AOX[3] in µg is calculated using the formula:

$$\text{Calibrated AOX} = \frac{\text{Instrument AOX} - \text{Blank AOX}}{\text{calibration factor}}$$

12.4 The AOX concentration of each dilution of the sample (Section 8.1) is calculated using the formula:

$$\text{AOX concentration} = \frac{\text{Calibrated AOX } (\mu g)}{\text{effective volume (mL) (Section 8.4)}}$$

Sample AOX concentration is the average of the AOX concentrations of each dilution[4]. This result in

---

[1] The calibration factor must be within the range of 0.95 to > 1.05 with a standard deviation of less than 0.03.

[2] The blank must be less than 1.0 µg AOX with a standard deviation less than 0.3 µg.

[3] Instrument AOX must be within the range of 2.5 to 40 µg.

[4] The AOX concentrations of both dilutions of a sample must agree within 10%:

$$-10 \leq \frac{100 \times 2x(A-B)}{A+B} \leq 10$$

A = AOX Concentration of dilution 1

B = AOX Concentration of dilution 2

μg/mL requires no conversion factor to be expressed in mg/L. If all of the specified criteria (see footnotes) have not been met, the results cannot be accepted.

12.5 The 2-chlorobenzoic acid spike recovery is calculated as follows.

$$\text{Recovery \%} = 100 \times \frac{(C-D)}{E \times F}$$

where C = calibrated AOX for spike sample.

D = AOX concentration of sample spiked multiplied by the effective volume of the spike sample.

E = concentration of 2-chlorobenzoic acid solution in μg AOX per μL.

F = volume of 2-chlorobenzoic acid solution, in μL, added.

The percent recovery of 2-chlorobenzoic acid as AOX must be within the range of 90 to 105% and must be reported with results.

13. Quality Assurance/Quality Control (QA/QC)

13.1 A daily calibration factor is calculated from the recovery factors of multiple 10.0 μL injections of trichlorophenol solutions directly into the sample boat (Section 10.2). The mean of the calibration factors must be no less than 0.95 and no more than 1.05 with a standard deviation of no more than 0.03.

13.1.2 QCA and QCB Analysis. QCA and QCB solutions are analyzed daily (10 μL injection directly into sample boat). The calibrated results are plotted on control charts. Control limits will be set when sufficient data is generated.

13.1.3 Full calibration curves must be developed after all major maintenance (Section 11.1). The slope of this curve must not be less than 0.95 and no more than 1.05, and a correlation factor of no less than 0.9995 must be achieved.

13.1.4 In the event of failure of either Section 13.1.1 or 13.1.2, any data generated must be rejected and the instrument must be brought back into control before any further analysis.

13.2 Analysis of Method Blanks.

13.2.1 At least two method blanks, as described in Section 8.7, must be analyzed per day. Any single determination over 1.0 µg or a spread of greater than 0.3 µg indicate that the method is out of control[1]. Steps must be taken to identify and remove the source of contamination before continuing with analysis.

13.3 Analysis of Duplicates and Replicates.

13.3.1 A minimum of one randomly selected sample per ten samples, or one per day (whichever is greater), is analyzed in duplicate. These results will be used to estimate the precision of the method. As data is generated precision limits will be determined.

13.3.2 All samples are analyzed at two different dilutions (Section 8.3). The two results must agree to within 10% or be rerun.

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[1] A blank must be the first method determination of the day, after test titrations and calibration determinations. High results may occur. If so, repeat the blank determination. If the second result falls within the acceptance range, disregard the first result, and continue analysis.

13.4 Analysis of Samples Fortified with 2-Chlorobenzoic Acid.

13.4.1 One dilution of each sample, randomly selected for duplicate analysis, is fortified with 20 µL of 2-chlorobenzoic acid solution and analyzed (Section 8.8). The recovery of AOX (Section 12.3) must be no less than 90% and no greater than 105%.

13.5 Analysis of Standard Reference Material.

13.5.1 The diverse nature and instability of the organic chlorine containing compounds in pulp mill effluents precludes the use of any standard reference material for pulp mill effluent AOX analysis.

13.6 Analysis of Reagent and Materials Used in Analysis.

13.6.1 Every lot of all materials and reagents used in the method are analyzed for chlorine prior to their use in AOX analysis.

13.7 Recording and Charting of QA/QC Data.

13.7.1 Current records and charts of all QA/QC charts will be maintained and made available to clients upon request.

13.8 General Laboratory Practices.

13.8.1 The working electrode is kept polished (sodium bicarbonate). If any discolouration or coating is observed during operation, analysis is stopped and the electrode is polished and the cell electrolyte is changed.

13.8.2 Analysis is only performed when the cell electrolyte is clear. When the electrolyte becomes cloudy, the cell is rehabilitated as above.

13.8.3 Cell electrolyte solution is prepared in large batches (lots) and tested before use. Uniformity of the batch is assumed. Changing cell electrolyte should not change cell efficiency.

13.8.4 Test titrations are performed after cell rehabilitation to oxidize trace amounts of impurity which may be present, and to ensure that the cell is operating correctly.

13.8.5 The outlet of the pyrolysis tube is visually inspected daily for soot or discolouration.

13.8.6 Joints are carefully inspected in the transfer/dehydration system.

13.8.7 Dilute nitric acid, nitrate solution and washing solutions are prepared in large lots to ensure uniformity of error.

13.8.7 New lots of GAC and membrane filter are tested for halide content prior to use in analysis.

14. Method Performance

Evaluation will be completed when sufficient data is available.

15. References

15.1 Scandanavian Pulp, Paper and Board Testing Committee, Standard Method SCAN-W 9:89, (1989).

15.2 DIN: DIN 38409H 14 Summarische Wirkungs and Stoffkenngro Ben (Gruppe H), Bestimmung der adsorbierbaren organisch gebundenen Haloger (AOX), Beuth-Verlag, Berlin (1985).

15.3 Methods for the Examination of Water and Waste water. Method 506 Organic Halogen (Dissolved). American Public Health Association, Washington, D.C. (1989).

15.4 L. Bauman and M.K. Stenstrom, Observations of Reaction between Organohalides and Sulfite, Environ. Sci. and Technol. 23, 232 (1989).

15.5 ASTM Standard Specification for Reagent Water. D1193-77 (Reapproved 1983).

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